

[54] **QUINOXALINES AND THEIR USE IN PHOTOGRAPHIC PROCESSES**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 799,020, May 20, 1977, abandoned.

[30] **Foreign Application Priority Data**

May 24, 1976 [CH] Switzerland 6521/76

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[52] U.S. Cl. **430/418; 430/430; 430/462**

[58] Field of Search 96/53, 73, 20

[56] **References Cited**

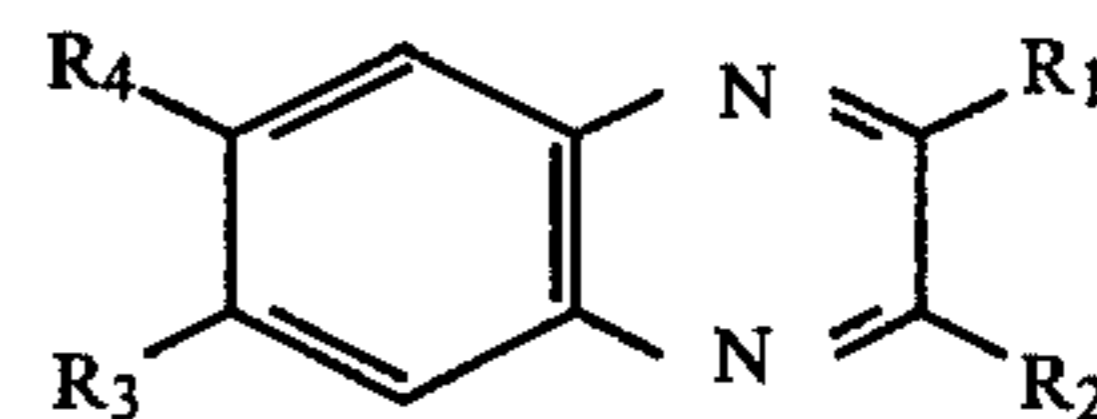
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[57] **ABSTRACT**

Quinoxalines of the formula



are provided, in which R₁ and R₂ independently are lower alkyl R₃ is lower alkyl, —CH₂OR₅, —CH₂NRR', —CH₂OCOR, —CH₂Cl, —CH₂Br, —CH₂SR, —CH₂O(CH₂)_pOR, —CH₂PO(OR₅)₂, —CH₂PO(OR₆)₂, —CH₂SO₃R₆, —O(CH₂)_mOR, —O(CH₂)_pSO₃R₆ or —(OCH₂CH₂)_nOAr, R₄ is hydrogen, lower alkyl or alkoxy when R₃ is other than lower alkyl, or R₄ is —OH, —NRR', —NHCOR, —NHCOAr', —NH-SO₂R₅ or —NHSO₂Ar', R and R' independently are hydrogen or lower alkyl, R₅ is lower alkyl, R₆ is hydrogen, an alkali metal cation or —N[⊕](R)₄, Ar is aryl or sulphonated aryl, Ar' is aryl or substituted aryl, m is 3 or 4, n is 1 to 3 and p is 2 to 4.

The quinoxalines are useful as bleach catalysts, especially as dye bleach catalysts, for the photographic silver dye bleach process.

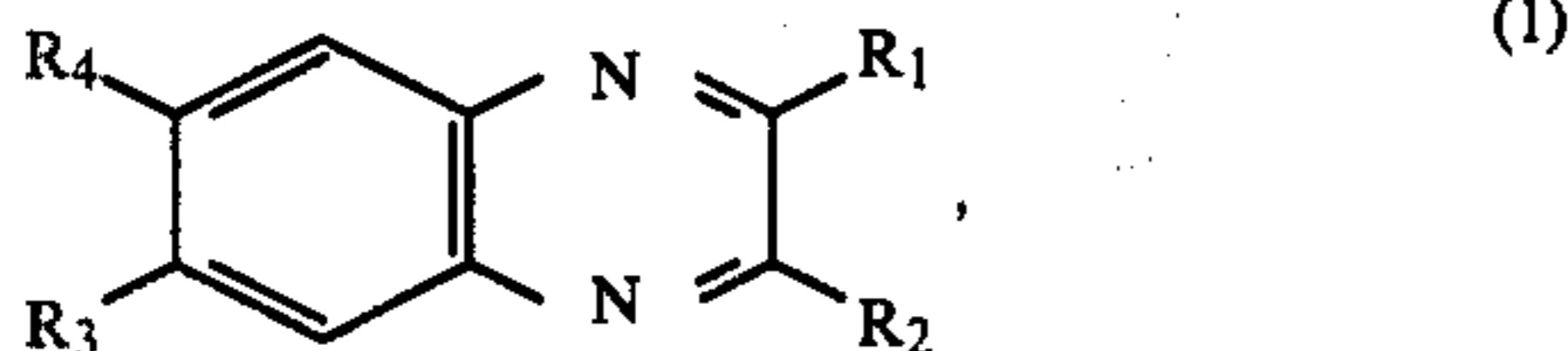
12 Claims, No Drawings

QUINOXALINES AND THEIR USE IN
PHOTOGRAPHIC PROCESSES

CROSS REFERENCE TO RELATED
APPLICATION

This a continuation-in-part of copending application Ser. No. 799,020, filed May 20, 1977 now abandoned.

The present invention relates to new quinoxalines of the formula



in which R_1 and R_2 independently are alkyl with 1 to 5 carbon atoms, R_3 is alkyl with 1 to 5 carbon atoms, $-\text{CH}_2\text{OR}_5$, $-\text{CH}_2\text{NRR}'$, $-\text{CH}_2\text{OCOR}$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{Br}$, $-\text{CH}_2\text{SR}$, $-\text{CH}_2\text{O}(\text{CH}_2)_p\text{OR}$, $-\text{CH}_2\text{PO}(\text{OR}_5)_2$, $-\text{CH}_2\text{PO}(\text{OR}_6)_2$, $-\text{CH}_2\text{SO}_3\text{R}_6$, $-\text{O}(\text{CH}_2)_m\text{OR}$, $-\text{O}(\text{CH}_2)_p\text{SO}_3\text{R}_6$ or $-\text{O}(\text{CH}_2\text{CH}_2)_n\text{OAr}$, R_4 is hydrogen or alkyl with 1 to 5 carbon atoms or alkoxy of 1 to 4 carbon atoms, when R_3 is other than an alkyl radical with 1 to 5 carbon atom, or R_4 is $-\text{OH}$, $-\text{NRR}'$, $-\text{NHCOR}$, $-\text{NHCOR}$, $-\text{NHCOAr}'$, $-\text{NHSO}_2\text{R}_5$ or $-\text{NHSO}_2\text{Ar}'$, R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms, R_5 is alkyl with 1 to 4 carbon atoms, R_6 is hydrogen, an alkali metal cation or $-\text{N}(\text{R})_4$, Ar is aryl or sulphonated aryl, Ar' is aryl or substituted aryl, m is 3 or 4, n is 1 to 3 and p is 2 to 4.

The radicals R_1 and R_2 independently are alkyl with 1 to 5 carbon atoms, such as, for example, methyl, ethyl, *n*- and iso-propyl, *n*- and iso-butyl, tert.-butyl or arnyl, ethyl and especially methyl being preferred.

If the radical R_3 is alkyl with 1 to 5 carbon atoms, these substituents can be the same as those indicated for R_1 and R_2 .

If R_3 represents a radical which contains R or R' as further substituents, these substituents as a rule denote hydrogen or straight-chain or branched alkyl with 1 to 4 carbon atoms, so that R_3 can be, for example, $-\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{N}(\text{CH}_3)_2$, $-\text{CH}_2\text{NHC}_4\text{H}_9$, $-\text{CH}_2\text{OCOH}$, $-\text{CH}_2\text{OCOCH}_3$, $-\text{CH}_2\text{OCOC}_2\text{H}_5$, $-\text{CH}_2\text{OCOC}_4\text{H}_9$, $-\text{CH}_2\text{SH}$, $-\text{CH}_2\text{SCH}_3$, $-\text{CH}_2\text{SC}_2\text{H}_5$, $-\text{CH}_2\text{SC}_3\text{H}_7$, $-\text{CH}_2\text{SC}_4\text{H}_9$, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}_2\text{H}_5$, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}_3\text{H}_7$, $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{OC}_4\text{H}_9$, $-\text{CH}_2\text{O}(\text{CH}_2)_3\text{OH}$, $-\text{CH}_2\text{O}(\text{CH}_2)_3\text{OCH}_3$, $-\text{CH}_2\text{O}(\text{CH}_2)_4\text{OCH}_3$, $-\text{CH}_2\text{O}(\text{CH}_2)_3\text{OC}_2\text{H}_5$, or $-\text{CH}_2\text{O}(\text{CH}_2)_3\text{OC}_4\text{H}_9$. The substituent R_5 can be straight-chain or branched alkyl with 1 to 4 carbon atoms, so that further possible radicals R_1 are, for example, $-\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{OC}_2\text{H}_5$, $-\text{CH}_2\text{OC}_3\text{H}_7$ (*n*- and iso-), $-\text{CH}_2\text{OC}_4\text{H}_9$ (*n*-, iso- or tertiary), $-\text{CH}_2\text{PO}(\text{OCH}_3)_2$, $-\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$, $-\text{CH}_2\text{PO}(\text{OC}_3\text{H}_7)$ or $-\text{CH}_2\text{PO}(\text{OC}_4\text{H}_9)$. As well as hydrogen, the substituent R_6 can be an alkali metal cation, for example a lithium, sodium or potassium cation, as well as an ammonium radical, such as, for example $-\text{N}^\oplus\text{H}_4$ or $-\text{N}^\oplus(\text{CH}_3)_4$.

Those radicals R_3 in which R and R' are hydrogen or methyl, R_5 is methyl and R_6 is hydrogen, a sodium or potassium cation or $-\text{N}^\oplus\text{H}_4$ are preferred.

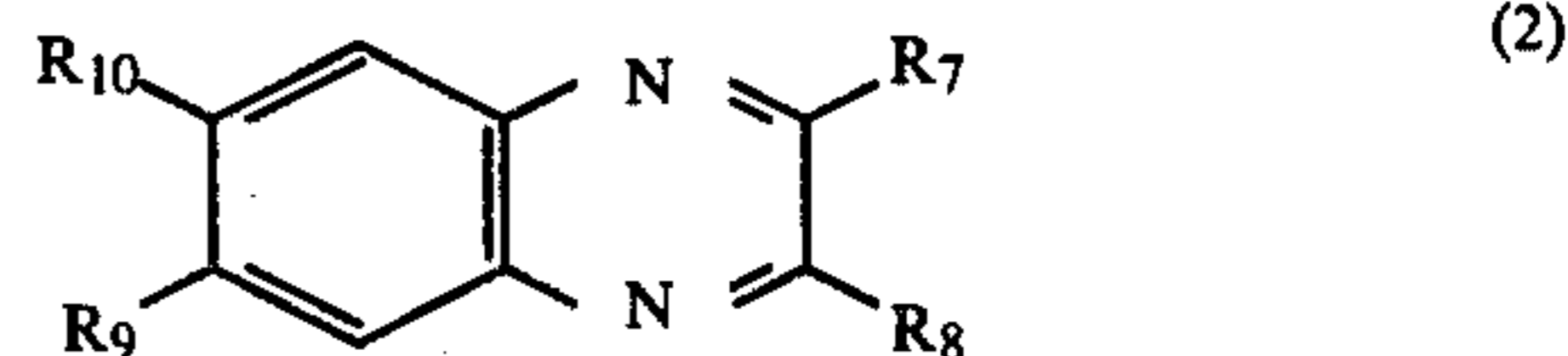
Further radicals R_3 can be $-\text{O}(\text{CH}_2)_3\text{OH}$, $-\text{O}(\text{CH}_2)_4\text{OH}$, $-\text{O}(\text{CH}_2)_3\text{OCH}_3$, $-\text{O}(\text{CH}_2)_3\text{OC}_2\text{H}_5$, $-\text{O}(\text{CH}_2)_3\text{OC}_3\text{H}_7$, $-\text{O}(\text{CH}_2)_3\text{OC}_4\text{H}_9$, and also $-\text{O}(\text{CH}_2\text{CH}_2)_1$

$-\text{OC}_6\text{H}_5$, $-(\text{OCH}_2\text{CH}_2)_{1-3}\text{OC}_6\text{H}_5\text{SO}_3\text{H}$ and $-\text{CH}_2\text{Cl}$ and $-\text{CH}_2\text{Br}$.

The radical R_4 is hydrogen, alkyl with 1 to 5 carbon atoms or alkoxy only when the radical R_3 is not an alkyl radical with 1 to 5 carbon atoms. If R_4 is alkyl, possible radicals are straight-chain and branched radicals, such as, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl or isoamyl. Further radicals R_4 can be, for example, $-\text{OH}$, $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$ or $-\text{OC}_3\text{H}_7$; $-\text{NH}_2$, $-\text{NHCH}_3$, $-\text{NHC}_2\text{H}_5$, $-\text{NHC}_3\text{H}_7$, $-\text{NHC}_4\text{H}_9$ or $-\text{N}(\text{CH}_3)_2$; $-\text{NHCOH}$, $-\text{NHCOC}_2\text{H}_5$, $-\text{NHCOC}_3\text{H}_7$ or $-\text{NHCOC}_4\text{H}_9$; $-\text{NHSO}_2\text{CH}_3$, $-\text{NHCOAr}'$ or $-\text{NH-SO}_2\text{Ar}'$, wherein Ar' is an aryl radical, especially a phenyl or naphthalene radical, or a substituted aryl radical, possible substituents being halogen, such as, in particular, fluorine, chlorine and bromine, lower alkyl and alkoxy, such as, for example, methyl and ethyl or methoxy and ethoxy, and also carboxyl ($-\text{COOH}$) or sulphonic acid ($-\text{SO}_3\text{H}$), it being possible for these also to be in the form of a salt, and carboxylic acid ester and sulphonic acid ester and nitro.

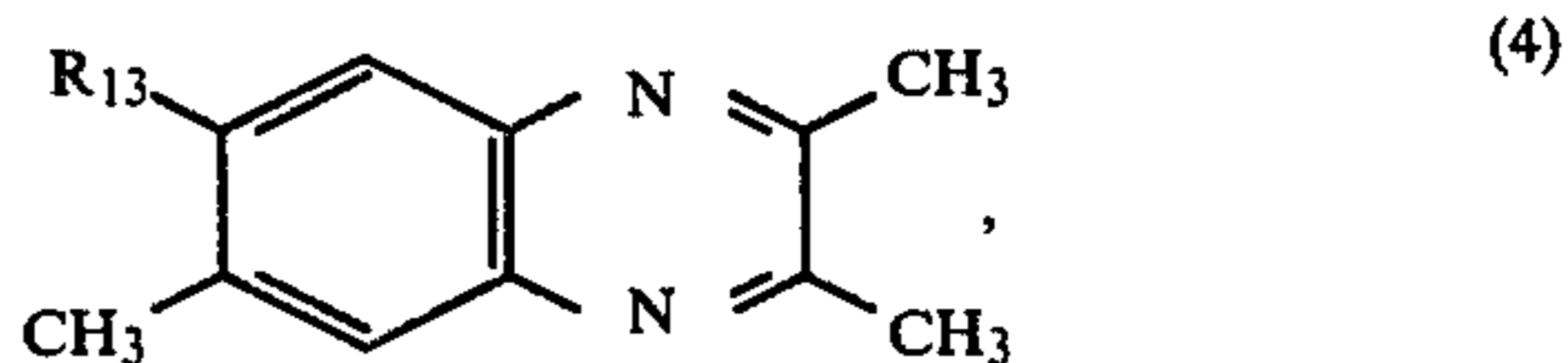
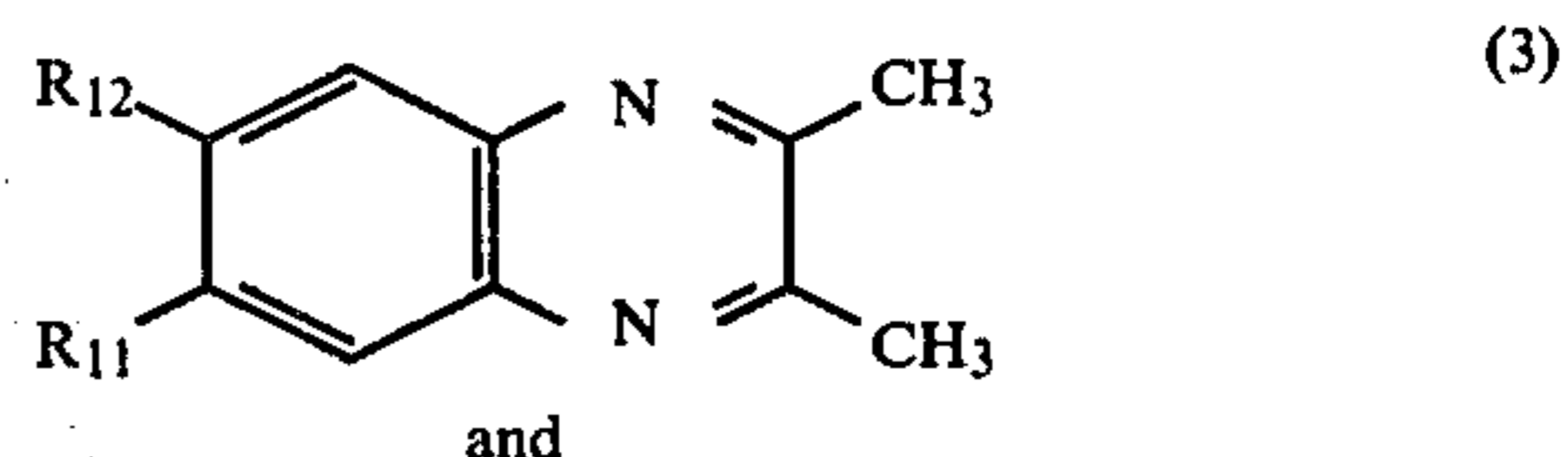
Those quinoxalines of the formula (1) in which R_1 and R_2 independently are methyl or ethyl, R_3 has the indicated meaning and R_4 is hydrogen or alkyl with 1 to 5 carbon atoms when R_3 is other than alkyl with 1 to 5 carbon atoms, or is $-\text{OH}$, $-\text{NRR}'$, $-\text{NHCOR}$ or $-\text{NHSO}_2\text{R}_5$, in which R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms are preferred.

The quinoxalines of the formula



in which R_7 and R_8 independently are methyl or ethyl, R_9 is alkyl with 1 to 5 carbon atoms and R_{10} is $-\text{OH}$, $-\text{NRR}'$, $-\text{NHCOR}$ or $-\text{NHSO}_2\text{R}_5$ and R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms and R_5 has the indicated meaning are of particular interest.

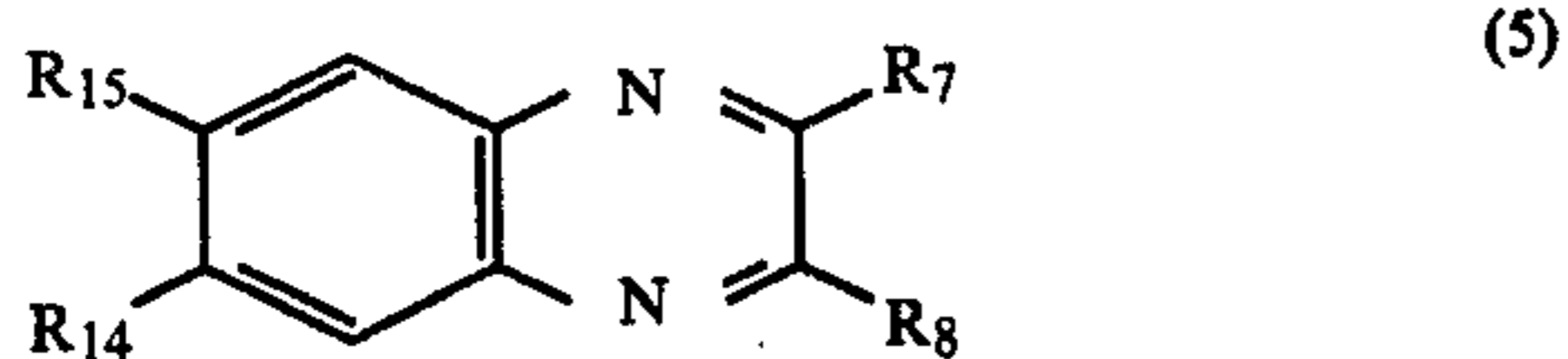
Particularly suitable quinoxalines also correspond to the formulae



in which R_{11} is methyl or ethyl, R_{12} is $-\text{OH}$, $-\text{NR}''\text{R}'''$, $-\text{NHCOC}_2\text{H}_5$ or $-\text{NHSO}_2\text{CH}_3$, R_{13} is $-\text{OH}$, NH_2 or $-\text{NHCOC}_2\text{H}_5$ and R'' and R''' independently are hydrogen or methyl.

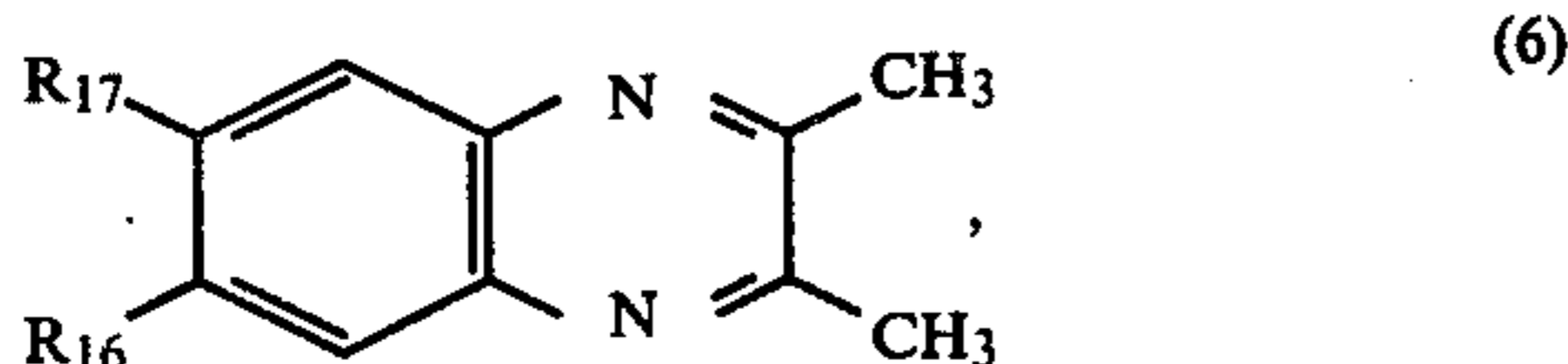
Furthermore, quinoxalines which correspond to the formula

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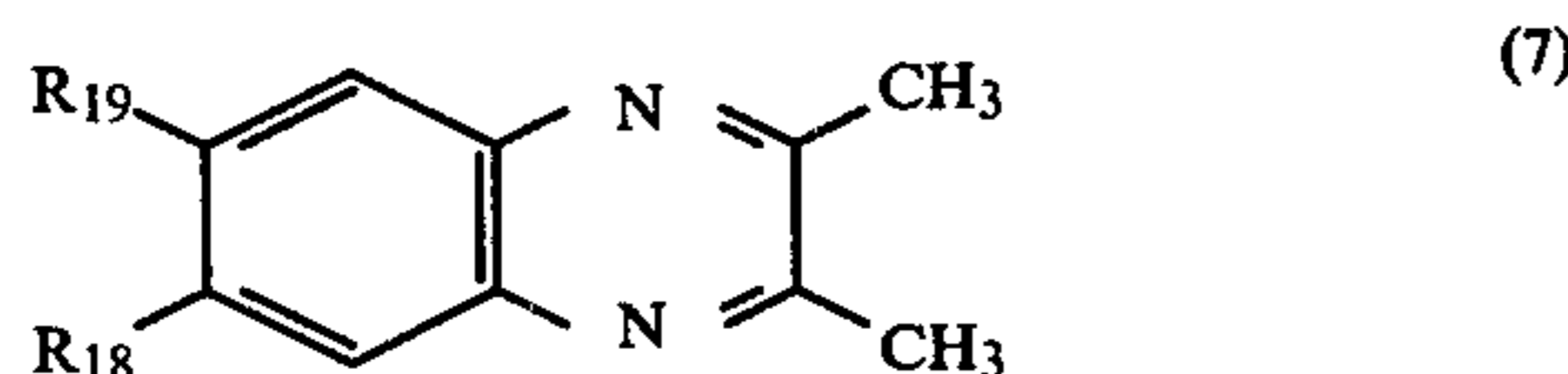


in which R_7 and R_8 have the indicated meanings, R_{14} is $-\text{CH}_2\text{OR}_5$, $-\text{CH}_2\text{NRR}'$, $-\text{CH}_2\text{OCOR}$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{Br}$, $-\text{CH}_2\text{SR}$, $-\text{CH}_2\text{O}(\text{CH}_2)_p\text{OR}$, $-\text{CH}_2\text{PO}(\text{OR}_5)_2$, $-\text{CH}_2\text{PO}(\text{OR}_6)_2$, $-\text{CH}_2\text{SO}_3\text{R}_6$, $-\text{O}(\text{CH}_2)_m\text{OR}$, $-\text{O}(\text{CH}_2)_p\text{SO}_3\text{R}_6$ or $-(\text{OCH}_2\text{CH}_2)_n\text{OAr}$, R_{15} is hydrogen or alkyl with 1 to 5 carbon atoms, $-\text{OH}$ or $-\text{OCH}_3$, R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms, R_5 is alkyl with 1 to 4 carbon atoms, R_6 is hydrogen, an alkali metal cation or $-\text{N}^\oplus(\text{R})_4$, Ar is aryl or sulphonated aryl, m is 3 or 4, n is 1 to 3 and p is 2 to 4, are also particularly valuable.

Particularly preferred quinoxalines of the formula (5) are, now, those compounds which correspond to the formulae



in which R_{16} is $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{Br}$, $-\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{OCOH}$, $-\text{CH}_2\text{OCOCH}_3$, $-\text{CH}_2\text{NR}''\text{R}'''$, $-\text{CH}_2\text{SO}_3\text{R}_6$, $-\text{CH}_2\text{O}(\text{CH}_2)_p\text{OH}$, $-\text{CH}_2\text{O}(\text{CH}_2)_p\text{OCH}_3$, $-\text{O}(\text{CH}_2)_p\text{SO}_3\text{R}_6$ or $-(\text{OCH}_2\text{CH}_2)_n\text{OAr}$, R_{17} is hydrogen, hydroxyl, methyl, ethyl or methoxy, R_6 is hydrogen, an alkali metal cation or $-\text{N}^\oplus(\text{R})_4$ and R is hydrogen or alkyl with 1 to 4 carbon atoms, R'' and R''' independently are hydrogen or methyl, Ar is aryl or sulphonated aryl, n is 1 to 3 and p is 2 to 4, and



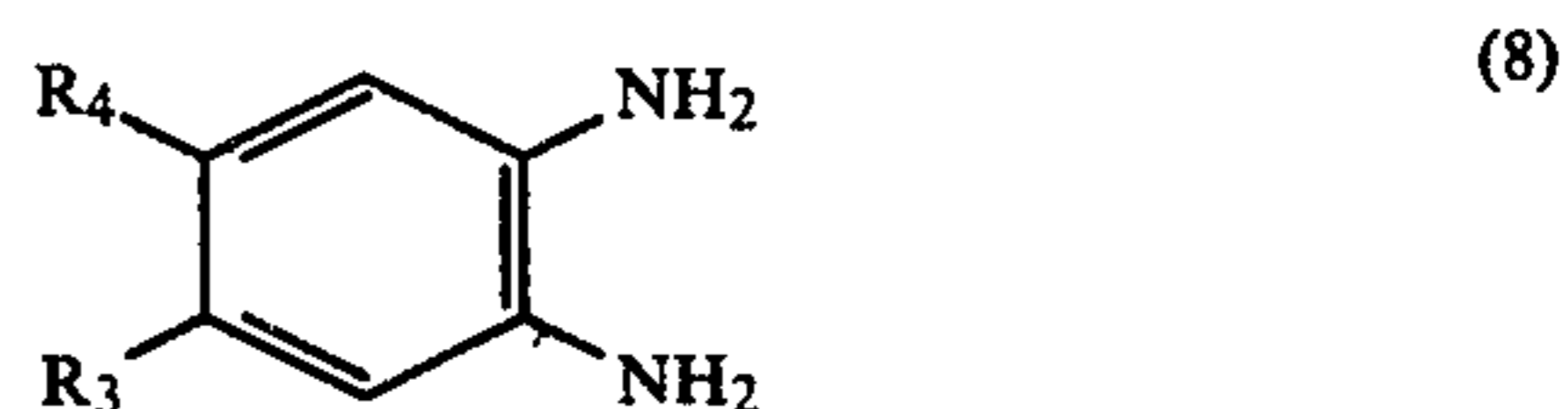
in which R_{18} is $-\text{CH}_2\text{Br}$, $-\text{CH}_2\text{OCH}_3$, $-\text{CH}_2\text{OCOH}$, $-\text{CH}_2\text{OCOCH}_3$, $-\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{SO}_3\text{R}_6$, $-\text{O}(\text{CH}_2)_p\text{SO}_3\text{R}_6$, $-(\text{OCH}_2\text{CH}_2)_n\text{OC}_6\text{H}_5$ or $-(\text{OCH}_2\text{CH}_2)_n\text{OC}_6\text{H}_4\text{SO}_3\text{R}_6$, R_{19} is hydrogen, methyl, hydroxyl or methoxy, R_6 is hydrogen, an alkali metal cation or $-\text{N}^\oplus(\text{R})_4$, R is hydrogen or alkyl with 1 to 4 carbon atoms, n is 1 to 3 and p is 2 to 4.

The quinoxalines of the formula (1) are appropriately manufactured in a manner which is in itself known (in this context compare J. C. E. Simpson, Condensed Pyridazine and Pyrazine Rings, in A. Weissberger, The Chemistry of Heterocyclic Compounds, J. Wiley & Sons, New York 1953, 203 et seq.; A. R. Katritzky, Advances in Heterocyclic Chemistry Volume 2, in G. W. H. Cheeseman, Recent Advances in Quinoxaline Chemistry, Academic Press, New York and London 1963, 203 et seq. and Y. T. Pratt, The Quinoxalines, in R. C. Elderfield, Heterocyclic Compounds Volume 6, J. Wiley & Sons, New York 1957, 455 et seq.) by a condensation reaction of an aromatic 1,2-diamine with a 1,2-dicarbonyl compound. In place of the diamine, it is also possible to use the corresponding, considerably more stable *o*-nitroaniline or the corresponding *o*-dinitro compound or the corresponding *o*-aryldiazaniline, which can be reduced to the desired diamine and then

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reacted, without intermediate isolation, to give the quinoxaline. Correspondingly substituted benzofuroxanes and their reduction products (benzofurazanes) can also be reduced via intermediate stages to 1,2-diamines (F. B. Mallory & S. P. Varimbi, J. Org. Chemistry 28, 1,656 et seq. (1963)) and the diamines thus accessible subjected to a condensation reaction to give quinoxalines. In place of the 1,2-dicarbonyl compound, α -oximinoketones can also be reacted with 1,2-diamines to give quinoxalines (in this context compare J. C. E. Simpson, loc. cit.).

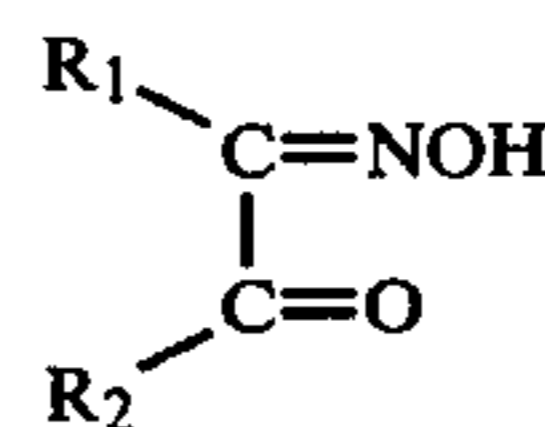
The present invention also relates to a process for the manufacture of the quinoxalines of the formula (1). The process is characterised in that aromatic diamines of the formula



in which R_3 and R_4 have the indicated meanings, are subjected to a condensation reaction with 1,2-dicarbonyl compounds of the formula



or α -oximinoketones of the formula

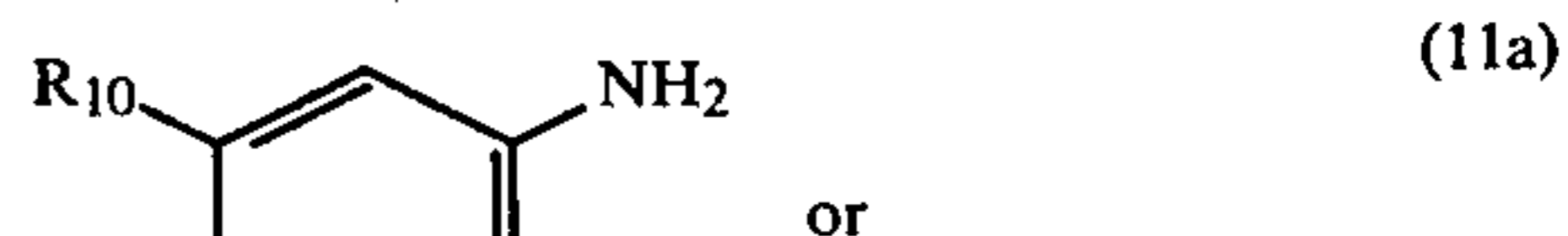


in which R_1 and R_2 have the indicated meanings.

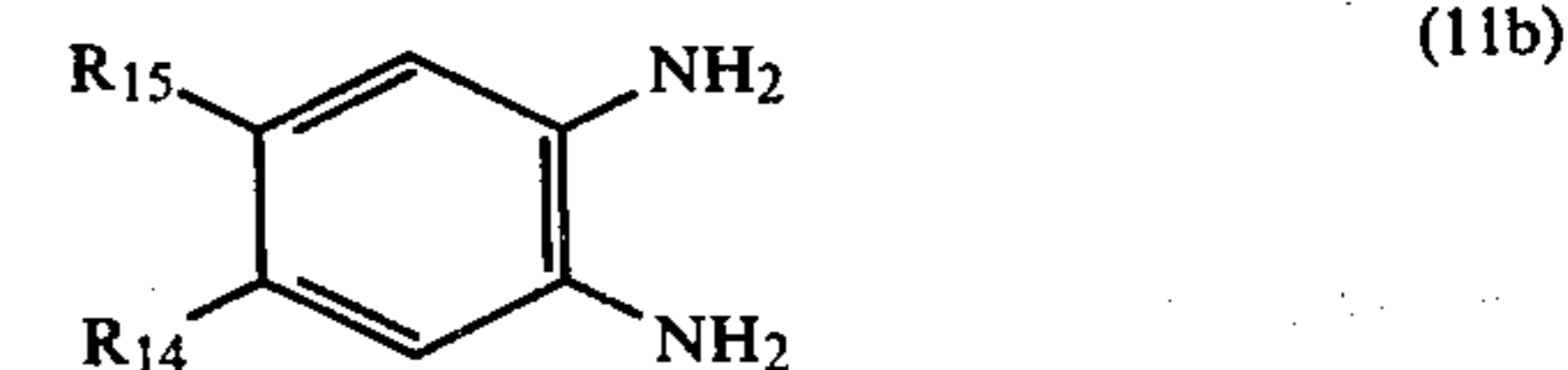
The condensation reaction is generally carried out in a solvent, for example, glacial acetic acid, 2-methoxyethanol, ethyl acetate, methanol or water, at temperatures of 5° to 100°C .

With this process the new compounds as a rule precipitate out when the reaction mixture is cooled after the end of the reaction; otherwise they are obtained in good yield by distilling off the solvent and filtering off as well as optionally recrystallising or purifying by chromatography.

The manufacture of the quinoxalines of the formulae (2) and (5) is carried out as indicated by subjecting an aromatic diamine of the formulae

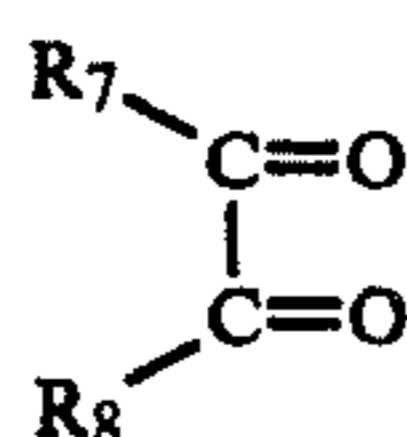


or

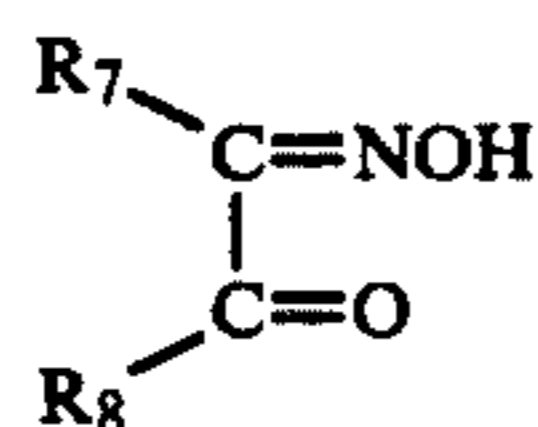


to a condensation reaction with a 1,2-dicarbonyl compound of the formula

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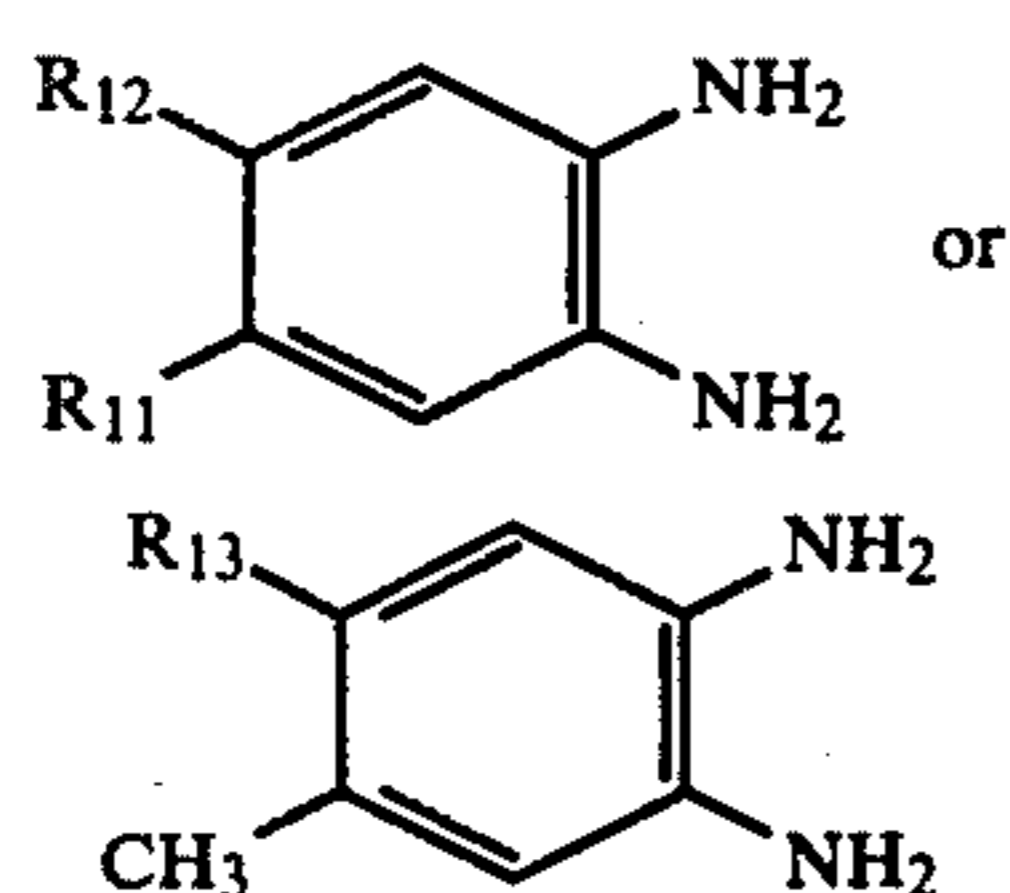


or with an α -oximinoketone of the formula

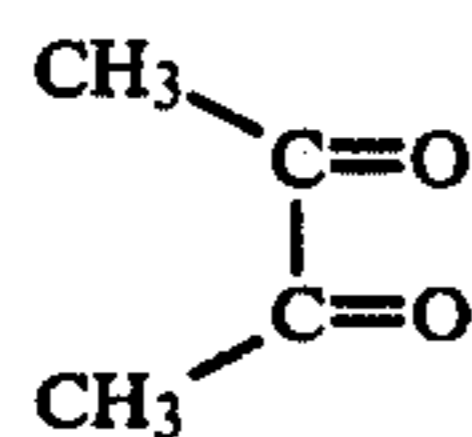


The radicals R_7 , R_8 , R_9 , R_{10} , R_{14} and R_{15} have the indicated meanings. 15

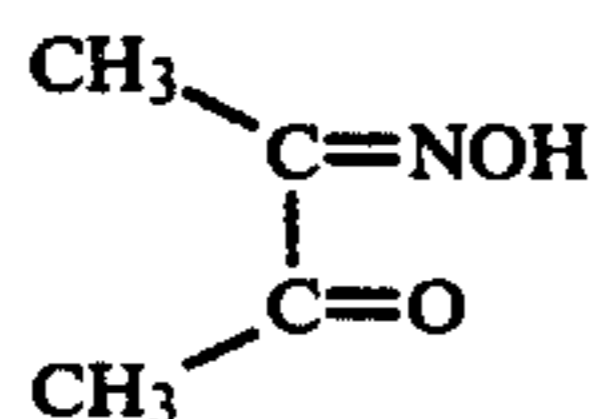
For the manufacture of the quinoxalines of the formulae (3) and (4), corresponding diamines of the formula



are reacted with diacetyl of the formula



or α -oximinobutan-2-one



The radicals R_{11} and R_{12} have the indicated meanings. Quinoxalines of the formulae (6) and (7) are manufactured analogously. 45

It has proved advantageous to manufacture quinoxalines of the formula (1) in which the radical R_3 is substituted in the α -position from the corresponding 6-methylquinoxalines by bromination or chlorination of the 6-methyl group and by subsequent replacement of the halogen atoms, using suitable Lewis bases. 50

Examples of Lewis bases which can be used are: primary and secondary amines, mercaptides, potassium phthalimide, guanidine, thiourea derivatives, alcohols, phosphites, sulphites, hydroxy compounds (hydroxides) and anions of carboxylic acids or sulphinic acids. 55

The alkoxy- and sulphoalkoxy-quinoxalines can appropriately be manufactured from the corresponding hydroxy compounds, for example 6-hydroxy-2,3-dimethylquinoxaline. These compounds can then be reacted in the customary manner in a suitable solvent (for example water, dimethylformamide or alcohols), in the presence of a base (for example potassium hydroxide or sodium hydroxide), with an alkylating agent (for example dimethyl sulphate or propanesultone). 60 65

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6-(4'-Sulphophenoxyalkoxy)-quinoxalines can preferably be obtained by sulphonation of the corresponding phenoxyalkoxyquinoxalines.

The quinoxalines which are substituted in the 7-position by carboxamide radicals or sulphonamide radicals can as a rule be obtained by acylation of the corresponding aminoquinoxalines with carboxylic acid anhydrides or carboxylic acid halides or sulphonic acid halides, especially the chlorides. 5

The quinoxalines can as a rule be obtained in better yield and higher purity if the condensation reaction is carried out in a nitrogen atmosphere. 10

Examples of starting materials which can be used for one of the said syntheses are the compounds named below:

1,2-Dicarbonyl compound, α -oximinoketones

Diacetyl, 3-oximinobutan-2-one, hexane-3,4-dione, 4-oximino-3-hexanone and 2,3-pentanedione. 20

Lewis bases

Sodium methylate, sodium ethylate, potassium methylate, potassium ethylate, potassium propylate, potassium isopropylate, potassium butylate, potassium isobutylate, potassium tertiary butylate, sodium mercaptide, potassium mercaptide, sodium methylmercaptide, potassium methylmercaptide, sodium ethylmercaptide, potassium ethylmercaptide, thiourea, sodium acetate, potassium xanthate, potassium acetate, sodium propionate, potassium propionate, sodium 3-methoxypropylate, potassium 3-methoxypropylate, sodium 4-methoxybutylate, potassium 4-methoxybutylate, sodium butyrate, potassium butyrate, sodium methoxyethylate, potassium 2-methoxyethylate, sodium 2-ethoxyethylate, potassium 2-ethoxyethylate, sodium monotetramethyleneglycolate, potassium monotetramethyleneglycolate, sodium monotrimethyleneglycolate, potassium monotrimethyleneglycolate, sodium monoglycolate, potassium monoglycolate, ammonia, potassium phthalimide, guanidine, dimethylamine, diethylamine, dipropylamine, methylamine, ethylamine, propylamine, sodium sulphite, potassium sulphite, water, sodium hydroxide, potassium hydroxide, trimethyl phosphite, triethyl phosphite, tributyl phosphite and tripropyl phosphite. 30 35 40 45

o-Nitroanilines and o-dinitrobenzenes, 1,2-diamines and o-aryazoanilines

1,2-Dinitro-4-(3-sulpho-1-propoxy)-benzene, 1,2-diamino-4-(3-sulpho-1-propoxy)-benzene, 1-amino-2-nitro-4-(3-sulpho-1-propoxy)-benzene, 2-amino-1-nitro-4-(3-sulpho-1-propoxy)-benzene, 1,2-dinitro-4-(2-sulpho-ethoxy)-benzene, 1,2-diamino-4-(2-sulphoethoxy)-benzene, 1-amino-2-nitro-4-(2-sulpho-ethoxy)-benzene, 2-amino-1-nitro-4-(2-sulphoethoxy)-benzene, 1,2-dinitro-4-(4-sulpho-1-butoxy)-benzene, 1,2-diamino-4-(4-sulpho-1-butoxy)-benzene, 1-amino-2-nitro-4-(4-sulpho-1-butoxy)-benzene, 2-amino-1-nitro-4-(4-sulpho-1-butoxy)-benzene, 1-methoxy-4,5-dinitro-2-(2-sulphoethoxy)-benzene, 1-methoxy-4,5-dinitro-2-(3-sulpho-1-propoxy)-benzene, 1-methoxy-4,5-dinitro-2-(4-sulpho-1-butoxy)-benzene, 4,5-diamino-1-methoxy-2-(2-sulphoethoxy)-benzene, 4,5-diamino-1-methoxy-2-(3-sulpho-1-propoxy)-benzene, 4,5-diamino-1-methoxy-2-(4-sulpho-1-butoxy)-benzene, (4)(5)-amino-1-methoxy-(5)(4)-nitro-2-(2-sulphoethoxy)-benzene, (4)(5)-amino-1-methoxy-(5)(4)-nitro-2-(3-sulpho-1-propoxy)-benzene, (4)(5)-amino-1-methoxy-(5)(4)-nitro-2-(4-sulpho-1-

butoxy)-benzene, 1-amino-4-hydroxymethyl-2-nitro-benzene, 1-hydroxymethyl-3,6-dinitrobenzene, 1,2-diamino-4-hydroxymethyl-benzene, 1-methoxymethyl-3,4-dinitro-benzene, 1,2-diamino-4-methoxymethyl-benzene, 1-amino-4-methoxymethyl-2-nitro-benzene, 2,4,5-triamino-toluene, 2,4-diamino-5-nitro-toluene, 2-amino-4,5-dinitro-toluene, 2-methylsulphonamido-4,5-dinitrotoluene, 2-acetamido-4,5-dinitro-toluene, 2,4-diamino-5-phenylazo-toluene, 2,4-diamino-5-(4-sulphophenylazo)-toluene, 2,4-diamino-5-(4-chlorophenylazo)-toluene, 2,4-diamino-5-(4-methylphenylazo)-toluene, 2-hydroxy-4,5-dinitro-toluene, 4,5-diamino-2-hydroxytoluene, 4-amino-2-hydroxy-5-phenylazo-toluene, 4-amino-2-hydroxy-5-(4-sulphophenylazo)-toluene, 4-amino-2-hydroxy-5-(4-chlorophenylazo)-toluene, 4-amino-2-hydroxy-5-(4-methylphenylazo)-toluene, 2-methoxy-4,5-dinitro-toluene, 4,5-diamino-2-methoxy-toluene, 4,5-dinitro-2-(2-sulphoethoxy)-toluene, 4,5-diamino-2-(2-sulphoethoxy)-toluene, 4,5-dinitro-2-(3-sulpho-1-propoxy)-toluene, 4,5-diamino-2-(3-sulpho-1-propoxy)-toluene, 4,5-dinitro-2-(4-sulpho-1-butoxy)-toluene, 4,5-diamino-2-(4-sulpho-1-butoxy)-toluene, 2-nitro-4-(2-phenoxyethoxy)-aniline, 3,4-dinitro-1-(2-phenoxyethoxy)-benzene and 2-nitro-4-[2-(4-sulphophenoxy)ethoxy]-benzene.

Quinoxalines (for halogenation of the side chains)

2,3,6-Trimethyl-quinoxaline and 2,3,6,7-tetramethyl-quinoxaline.

Amino- and hydroxy-quinoxalines

(for example for alkylation and acylation)

6-Hydroxy-2,3-dimethyl-quinoxaline, 6-hydroxy-2,3,7-trimethyl-quinoxaline, 6-amino-2,3,7-trimethyl-quinoxaline and 6-hydroxy-7-methoxy-2,3-dimethyl-quinoxaline.

Alkylating agents, acylating agents and sulphonic acid chlorides

The sodium salt of 2-bromo-ethanesulphonic acid, the sodium salt of 2-chloro-ethanesulphonic acid, propane-sultone, butanesultone, methyl iodide, ethyl iodide, ethyl bromide, acetic anhydride, acetyl chloride, methanesulphonyl chloride, benzenesulphonyl chloride and p-toluenesulphonyl chloride.

Quinoxalines

(for example for sulphonation)

2,3-Dimethyl-6-(2-phenoxy-ethoxy)-quinoxaline.

The quinoxalines of the formula (1) can be used in a processing bath, preferably an acid bleach bath, as bleach catalysts for the silver dye bleach process and especially in an acid dye bleach bath as dye bleach catalysts.

They are particularly readily soluble in acid baths and have an excellent action as dye bleach catalysts.

6-(Hydroxymethyl)-2,3-dimethylquinoxaline (C.A. 51, 433a) and 6-(2-hydroxyethoxy)-2,3-dimethylquinoxaline (C.A. 48, 884d) are dye bleach catalysts which also have a good action.

They can be used either on their own or in the presence of other customary dye bleach catalysts. It is also possible for different quinoxalines of the formula (1) to be used at the same time in the dye bleach bath. Finally, it is also possible to employ the quinoxalines of the formula (1) together with other measures which promote dye bleaching, such as, for example, by adding organic solvents or bleaching accelerators.

The quinoxalines of the formula (1) are, furthermore, also suitable for processes for the production of coloured photographic images by the silver dye bleach process as well as also for processes for rapid processing of silver dye bleach materials. In these processes, for example, the dye bleach bath, the silver bleach bath and, optionally, also the fixing bath are combined.

As a rule, these combined baths then contain bleaching accelerators, such as, for example, phosphines, oxidising agents and antioxidants (compare DT-OS No. 2,448,433) in addition to the said quinoxalines.

The present invention thus also relates to a process for the production of coloured photographic images by the silver dye bleach process on materials which contain, on a substrate, at least one silver halide emulsion layer with a dye-stuff which can be bleached image-wise, by exposure and subsequent processing by developing the silver image, dye bleaching, silver bleaching, silver fixing and washing, wherein the dye bleaching and/or silver bleaching is carried out in the presence of at least one quinoxaline of the formula (1) as the bleach catalyst, as well as also to a process for the rapid processing of silver dye bleach materials which comprises the following process steps (1) silver developing, (2) dye bleaching and silver bleaching, (3) silver fixing and (4) washing.

The latter process is characterised in that, using treatment baths corresponding to the treatment stages (1) to (4), and using them in the sequence (1) to (4), a bleach bath which contains (a) a strong acid, (b) a water-soluble iodide, (c) a water-soluble oxidising agent, (d) an antioxidant and (e) as the dye bleach catalyst, a quinoxaline of the formula (1), preferably in an amount of 0.5 to 5 g per liter, and (f) optionally a bleach accelerator is used for the combined dye bleaching and silver bleaching (2) and that the entire processing, from entry into the first bath (1) to leaving the final bath, is carried out at temperatures of 20° to 90° C.

Moreover, the processing can also be so carried out that the entire processing, from entry into the first bath (1) to leaving the final bath, takes at most 10 minutes and the dwell time in the individual baths is at most 2 minutes.

The invention also relates to photographic processing baths, especially dye bleach baths or combined dye bleach and silver bleach baths, for the silver dye bleach process which contain, as the bleach catalyst, at least one quinoxaline of the formula (1). In general, the aqueous dye bleach formulations required for the processing are allowed to act on the material in the form of dilute aqueous solutions which contain components (a) to (e) and optionally (f).

However, other methods, for example use in paste form, are also conceivable. The temperature of the baths during processing, and especially also the temperature of the bleach bath, can in general be between 20° and 60° C. and, of course, the requisite processing time is shorter at a higher temperature than at a lower temperature.

The aqueous bleaching formulation according to the present invention can also be prepared in the form of a liquid concentrate, especially an aqueous concentrate, and, because of its good stability, can be stored for a prolonged period. It is advantageous to use, for example, two liquid concentrates, of which one contains the strong acid (a) and the oxidising agent (c) and the other contains the remaining components (b), (d), (e) and optionally (f), it being possible to add an additional

solvent, such as ethyl alcohol or propyl alcohol, ethylene glycol methyl ether or ethylene glycol ethyl ether, to the latter concentrate in order to improve the solubility, especially of component (e).

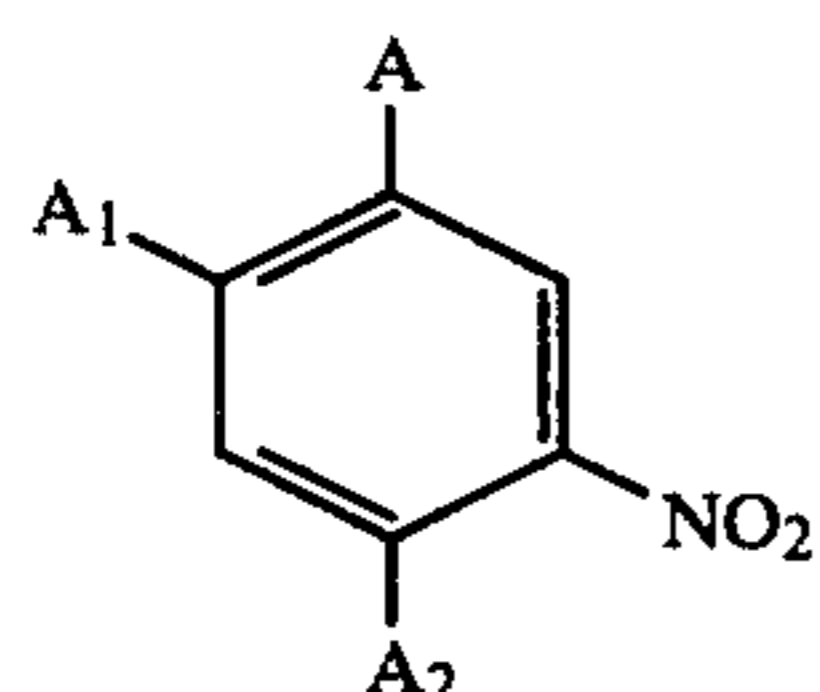
These concentrates can optionally be diluted by dilution with water or with a mixture of water and an organic solvent.

For silver developing in process step (1) it is possible to use baths of customary composition, for example those which contain hydroquinone and, if desired, additionally 1-phenyl-3-pyrazolidinone, as the developer substance.

The bleach bath (2) preferably contains sulphuric acid or sulphamic acid as the strong acid. The pH value of the bleach bath (2) is, in particular, not greater than 2 and preferably not greater than 1. The water-soluble iodides are as a rule alkali metal iodides, especially sodium iodide and potassium iodide. The amount of iodide is about 2 to 50 g/l of bleach bath.

Water-soluble, aromatic nitro and dinitro compounds are appropriately used as the oxidising agent. The use of such oxidising agents with a view to thus influencing the colour balance and the contrast in the images produced by the dye bleach process has already been described in German Pat. No. 735,672, in British Pat. Nos. 539,190 and 539,509 and in Japanese Pat. Publication No. 22,673/69.

Particularly advantageous oxidising agents are the compounds of the formula



in which A is $-\text{CO}_2\text{M}$ or $-\text{SO}_3\text{M}$, A_1 is hydrogen, hydroxyl, amino (NH_2), methyl or methoxy, A_2 is hydrogen, methyl, methoxy or trifluoromethyl and M is hydrogen, an alkali metal cation or $-\text{N}^{\oplus}(\text{R})_4$, in which R has the indicated meaning.

Examples of oxidising agents which can be used are the following aromatic nitro compounds: 3-nitrobenzenesulphonic acid, 3-nitrobenzoic acid, 2-amino-5-nitrobenzoic acid, 2-amino-5-nitrobenzenesulphonic acid, 2-amino-4-methyl-5-nitrobenzenesulphonic acid, 2-amino-4-methoxy-5-nitrobenzenesulphonic acid, 4-nitrophenol-2-sulphonic acid, 2-hydroxy-5-nitrobenzoic acid, 5-methyl-4-nitrophenol-2-sulphonic acid, 4-nitrotoluene-2-sulphonic acid, 4-nitroanisole-2-sulphonic acid, 2,4-dimethyl-5-nitrobenzenesulphonic acid, 5-methyl-4-nitroanisole-2-sulphonic acid and 2-nitrotoluene-4-sulphonic acid; the following products can also be used: 2-amino-4-trifluoromethyl-5-nitrobenzenesulphonic acid, 2-amino-3-methyl-5-nitrobenzenesulphonic acid, 2-amino-3-methoxy-5-nitrobenzenesulphonic acid, 2-amino-5-methoxy-3-nitrobenzenesulphonic acid, 3-amino-4-methyl-5-nitrobenzenesulphonic acid, 2,4-diamino-5-nitrobenzenesulphonic acid, 2-amino-4-nitrobenzenesulphonic acid, 2,4-diamino-5-nitrobenzenesulphonic acid, 2-amino-4-nitrobenzenesulphonic acid, 2-amino-5-methoxy-4-nitrobenzenesulphonic acid, 3-amino-4-methoxy-6-nitrobenzenesulphonic acid, 2-amino-5-methyl-3-nitrobenzenesulphonic acid, 3-nitroaniline, 2-methyl-4-nitroaniline, 3-amino-7-nitronaphthalene-1,5-disulphonic acid, 2-amino-4-nitrophenol-6-sulphonic acid, 2-nitrophenol-4-

sulphonic acid, 2-nitroanisole-4-sulphonic acid, 4-chloro-3-nitrobenzenesulphonic acid, 2-chloro-5-nitrobenzenesulphonic acid, 2,4-dinitrobenzenesulphonic acid, 2,6-dinitrotoluene-4-sulphonic acid, 2,4-dimethyl-3-nitrobenzenesulphonic acid, 2,4,6-trimethyl-3-nitrobenzenesulphonic acid, 2-amino-4-chloro-5-nitrobenzenesulphonic acid, 2-amino-3-chloro-5-nitrobenzenesulphonic acid, 2-nitrobenzoic acid, 3-nitrophthalic acid, 4-nitrophthalic acid, 3-[3'-nitrophenoxy]propanesulphonic acid and (2'-dimethylamino)ethyl 4-nitrobenzoate.

The nitrobenzenecarboxylic acids or nitrobenzenesulphonic acids can be used either in the form of free acids or in the form of their metal salts, especially in the form of the alkali metal salts or alkaline earth metal salts, or in the form of ammonium salts.

The amount of oxidising agent in the bleach bath can be in the range from 1 to 30 g/l.

Organic mercapto compounds are advantageously used as antioxidants. It has proved particularly advantageous to use the compounds of the formulae



in which q denotes an integer with a value of 2 to 12, B denotes a sulphonic acid group or carboxylic acid group and m denotes one of the numbers 3 and 4. Mercapto compounds which can be used as antioxidants are described in DT-OS No. 2,258,076 and in DT-OS No. 2,423,814. Other antioxidants are e.g. thioglycerol or thiomalic acid or reductones such as ascorbic acid (U.S. Pat. Specification No. 3,620,744). The amount of antioxidant is about 0.5 to 10 g/l.

The pH value of the bleach bath (2) should be less than 2 and this can be achieved without difficulty by the presence of sulphuric acid or sulphamic acid, which have already been mentioned. The temperature of the bleach bath, and also of the other treatment baths, is 20° to 90° C. In general it is advantageous to work at temperatures of not more than 60° C. The ratios of the substances (a), (b), (c) and (d) present in the bleach bath can vary within rather wide limits and are appropriately chosen analogously to the ratios for known methods. It is advantageous if the bleach baths contain the indicated, relatively high amount of 0.5 to 5 g of dye bleach catalyst per liter of bath liquid.

The silver fixing bath can be of known and customary composition. The fixer used is, for example, sodium thiosulphate or, advantageously, ammonium thiosulphate, if desired with additives such as sodium bisulphite and/or sodium metabisulphite.

All the baths can contain additives, such as hardeners, wetting agents, optical brighteners and UV-stabilisers.

The process for the rapid processing of silver dye bleach materials can be used, for example, in the production of positive coloured images in automatic copying or recording machines or in the rapid processing of other silver dye bleach materials, such as, for example, for scientific recording and industrial purposes, for example coloured X-ray screen photography.

A transparent, metallic-reflecting material or, preferably, white-opaque material, the carrier of which is not able to absorb any liquid from the baths, can be used as the silver dye bleach material.

The carrier can consist, for example, of optionally pigmented cellulose triacetate or polyester. If it consists of a paper felt this must be lacquer-coated or coated with polyethylene on both sides. The light-sensitive layers are located on at least one side of this carrier, preferably in the known arrangement, that is to say at the bottom a red-sensitised silver halide emulsion layer which contains a cyan azo dye-stuff, above this a green-sensitised silver halide emulsion layer which contains a magenta azo dyestuff and on the top a blue-sensitive silver halide emulsion layer which contains a yellow azo dyestuff. The material can also contain sublayers, intermediate layers, filter layers and protective layers, but the total thickness of the layers as a rule should not exceed 20 μ .

Manufacturing instructions

General instruction A

Quinoxalines manufactured from an aromatic 1,2-diamine, a *o*-nitroaniline compound or a *o*-dinitrobenzene derivative and a 1,2-dicarbonyl compound

A substituted *o*-dinitrobenzene derivative or the corresponding *o*-nitroaniline compound is dissolved, or merely suspended, in a suitable solvent such as, for example, ethyl acetate, methanol, ethanol, glacial acetic acid, dimethylformamide, 2-methoxyethanol, 2-ethoxyethanol or water, 1 to 10 percent by weight of a hydrogenation catalyst, such as, for example, a 10% strength palladium-on-charcoal catalyst, are added and the hydrogenation is carried out under normal pressure, with initial warming if necessary. After the reaction has ended, the catalyst is filtered off under nitrogen and at least the equimolar amount of the corresponding diketone is added, under nitrogen, to the filtrate, which is cooled to 0° C. to 10° C. if necessary; in most cases a deepening of the colour takes place when this addition is made. The mixture is then stirred, with warming if necessary, until the reaction has ended and the desired substance is isolated. The product can be purified by recrystallisation from a suitable solvent, distillation or, if necessary, by chromatography or sublimation.

In some cases, sodium hydrosulphite in alkaline solution is used as the reducing agent in order to reduce the *o*-dinitrobenzene derivative or the corresponding *o*-nitroaniline compound to the 1,2-diaminobenzene derivative.

If the corresponding *o*-phenylenediamine is easily accessible and in sufficient purity, it is, as described, subjected direct or in the form of its hydrochloride in a suitable solvent, under nitrogen, to a condensation reaction with the diketone. When the hydrochloride is used, it is advisable, in order to neutralise the hydrochloric acid liberated, to add a corresponding amount of sodium acetate or potassium acetate. The compound which are obtained in this way are listed in Table I.

Preparation Example A-1: (Compound No. 101)

The ammonium salt of
2,3-dimethyl-6-(3-sulpho-1-propoxy)-7-methoxyquinoxaline,

Preparation of 1-methoxy-4,5-dinitro-2-(3-sulpho-1-propoxy)-benzene:

Guaiacol is alkylated in dimethylformamide, in the presence of the stoichiometric amount of 30% strength aqueous sodium hydroxide solution, with propanesultone (yield: 87%). The *o*-(3-sulpho-1-propoxy)-anisole

(sodium salt) is converted, in quantitative yield, into the barium salt using a barium chloride solution.

The free acid is liberated by adding the equimolar amount of sulphuric acid, the barium sulphate is then filtered off and the water is removed. The residue is dissolved in an acetic acid/acetic anhydride mixture and nitrated with an excess of 96% strength nitric acid at 100° C. The reaction mixture is discharged into cold water. The pH value of the solution thus obtained is adjusted to 5 with 30% strength aqueous sodium hydroxide solution and an excess of barium chloride is added to the mixture. The barium salt of 1-methoxy-4,5-dinitro-2-(3-sulpho-1-propoxy)-benzene precipitates out. The product is filtered off, washed with acetone and dried in vacuo at 60° C.

Yield: 84% of theory. Analysis, calculated: Ba 17.0; S 7.94; found: Ba 15.8; S 7.50.

The free acid is liberated using the equimolar amount of sulphuric acid, the barium sulphate thus formed is filtered off and the water is evaporated. The residue is dissolved in methanol; an excess of an aqueous 28% strength ammonia solution is then added dropwise. The ammonium salt separates out as a yellow precipitate. The precipitate is filtered off, washed with methanol and isopropanol and dried in vacuo at 60° C. The product is obtained in a yield of 71% of theory. Melting point: 243° to 245° C.; the NMR and infrared spectra correspond to the indicated structure.

The compound obtained in this way is reduced as described in instruction A and the reaction product is reacted with diacetyl. The compound of the formula (101) is obtained in 60% yield.

Melting point: 223° to 227° C.

The IR and NMR spectra and also the elementary analysis correspond to the indicated structure.

Preparation Example A-2: (Compound No. 102)

1-Amino-2-nitro-4-(2-phenoxy-ethoxy)-benzene

This compound is prepared in a manner which is in itself known (see J. Scarborough, J. Chem. Soc. 1929, 2366 "Preparation of 3-nitro-4-amino-diphenyl ether").

1-Chloro-4-nitrobenzene is reacted in dimethylsulphoxide, in the presence of a base, with ethylene glycol monophenyl ether: 1-nitro-4-(2-phenoxy-ethoxy)-benzene is obtained in 87% yield.

(Melting point: 86° to 87° C.).

1-Nitro-4-(2-phenoxy-ethoxy)-benzene is reduced and the resulting amine is heated in acetic anhydride and glacial acetic acid and nitrated with 70% strength nitric acid. 1-Acetamido-2-nitro-4-(2-phenoxy-ethoxy)-benzene is obtained in 90% yield (melting point: 104° to 106° C.). The amide is hydrolysed with potassium hydroxide in ethanol and the desired nitroamine is obtained in 98% yield (melting point 121° to 123° C.).

The nitroamine thus obtained is reduced and the reaction product is reacted with diacetyl. (Compare Instruction A). The compound of the formula (102) is obtained in 90% yield.

Melting point: 114° to 115° C.

The IR and NMR spectra as well as the elementary analysis correspond to the indicated structure.

General Instruction B

Quinoxaline prepared from an *o*-arylazoaniline compound

A correspondingly substituted aniline, usually a substituted *m*-phenylenediamine or a substituted *m*-amino-

phenol, is coupled with a suitable aromatic diazonium salt, such as, for example, 4-diazobenzenesulphonic acid. In general, the azo grouping in the resulting dyestuff is reduced, without isolation of the dyestuff, using sodium hyposulphite in alkaline solution at temperatures between 40° and 90° C., to give the amine. The pH value of the reaction mixture is brought to 5 to 6 with hydrochloric acid or acetic acid and the diamine formed is then subjected to a condensation reaction with at least the equimolar amount of a diketone, at temperatures of 25° C. to 70° C.

The desired compound is then isolated. The product can be purified by recrystallisation from a suitable solvent, by distillation or, if necessary, by chromatography or sublimation.

If phenyldiazonium salts, 4-methylbenzenediazonium salts or 4-chlorobenzenediazonium salts are used, in place of 4-diazobenzenesulphonic acid, for the coupling reaction, the azo grouping formed can also be hydrogenated catalytically to give the amine. (Compare Instruction A).

Compounds which have been synthesised according to these instructions are listed in Table II.

Preparation Example B-1: (Compound No. 104)

6-Amino-2,3,7-trimethyl-quinoxaline

122 g (1 mol) of 2,4-diaminotoluene are mixed with 700 ml of water, 300 g of ice and 83 ml of concentrated hydrochloric acid. The solution is cooled to 0° C. and 218.5 g (1 mol) of moistened 4-diazobenzenesulphonic acid (titre: 77%) are added in portions, whilst stirring.

A red dyestuff forms spontaneously. The pH value of the mixture is kept at 2 to 3 by adding a 30% strength sodium acetate solution. The red suspension is stirred for two hours at 5° C. 200 ml of 30% strength sodium hydroxide solution are then added; the mixture thus obtained is then introduced into a solution of 500 g of sodium hyposulphite monohydrate, 100 ml of 30% strength sodium hydroxide solution and 1,800 ml of water. The mixture is stirred and heated to 70° C. for 30 minutes. The deep red solution loses its colour and a clear brown-yellow solution is obtained. The solution is cooled to 30° C. and the pH value is adjusted to 5 to 6 by adding 300 ml of glacial acetic acid. 90 g (1.05 mols) of diacetyl are added dropwise and the resulting mixture is stirred for 60 minutes. The desired product separates out as a yellow precipitate and this is filtered off. The crude product is suspended in 1,500 ml of water and the suspension is stirred for 10 minutes and then filtered. The resulting product is dried in vacuo at 60° C.

Yield: 141 g (75% of theory).

Melting point: 226° to 228° C.

The IR and NMR spectra and the elementary analysis correspond to the indicated structure.

General Instruction C:

Quinoxalines manufactured by nucleophilic substitution of α -halogenomethylquinoxalines using Lewis bases:

A 6-(α -halogenomethyl)-quinoxaline is dissolved, or merely suspended, in a suitable solvent, such as, for example, methanol, ethanol, 2-methoxyethanol, 2-ethoxyethanol, dimethylformamide, dimethylsulphox-

ide, acetonitrile, water, glycol, toluene, chlorobenzene, sulpholane or formamide. The Lewis base, optionally in a suitable solvent, is added to the solution of the 6-(α -halogenomethyl)-quinoxaline, or a solution or suspension of the 6-(α -halogenomethyl)-quinoxaline is added to the solution of the Lewis base. The mixture thus obtained is, if necessary, heated to the desired temperature and the compound formed is isolated. The product is purified by the customary processes.

The compounds which are manufactured according to this instruction is listed in Table III.

General Instruction D:

Alkylation or acylation of hydroxy- or amino-quinoxalines

The alkali metal salt of a 6-hydroxyquinoxaline, or a 6-aminoquinoxaline, is dissolved or suspended in a suitable solvent (for example water, dimethylformamide, methanol, ethanol or methylcellosolve or, respectively, dimethylformamide, dimethoxyethane, acetone, pyridine, toluene or chlorobenzene), the solution or suspension is mixed with the alkylating or acylating reagent and the whole is heated to the desired reaction temperature. The product is isolated and purified if necessary.

The compounds obtained according to this instruction are listed in Table IV.

Preparation Example D-1: (Compound No. 112)

The sodium salt of

2,3-dimethyl-6-(3-sulpho-1-propoxy)quinoxaline

8.7 g (50 mmols) of 6-hydroxy-2,3-dimethylquinoxaline are dissolved in 50 ml of dimethylformamide and 6.6 g (50 mmols) of 30% strength sodium hydroxide solution are added. The solution is stirred for 15 minutes and 6.7 g (55 mmols) of propanesultone are then added. The mixture is heated to 65° C. for two hours. It is allowed to cool to room temperature; thereupon the desired product separates as a white precipitate. The mixture is cooled to 0° C. and the precipitate is filtered off and washed with 1,2-dimethoxyethane. The product is dried in vacuo at 60° C. 9.7 g (58% of theory) of a white powder are obtained (the product contains 1 mol of H₂O).

The NMR and infrared spectra correspond to the indicated structure.

Further Manufacturing Instructions (E)

Preparation Example E-1: (Compound No. 116)

6-(Bromomethyl)-2,3-dimethoxyquinoxaline

is obtained by free radical bromination of 2,3,6-trimethylquinoxaline by means of N-bromosuccinimide. Carbon tetrachloride is used as the solvent and α,α' -azobisisobutyronitrile is used as the catalyst.

Preparation Example E-2: (Compound No. 115)

2,3-Dimethyl-6-[2-(4-sulphophenoxy)-ethoxy]-quinoxaline

is obtained from 2,3-dimethyl-6-(2-phenoxy-ethoxy)-quinoxaline (compound 102) by sulphonation using 10% strength oleum.

TABLE I

No.	Compound	Starting materials	Reducing agent
101			(CH ₃ CO) ₂ H ₂ /Pd-C/Pt (H ₂ O-CH ₃ OCH ₂ CH ₂ OH) (80:20)
102			(CH ₃ CO) ₂ H ₂ /Pd-C CH ₃ COOH
103			(CH ₃ CO) ₂ Na ₂ S ₂ O ₄ H ₂ O/NaOH

No.	Compound	Isolation	Yield %	Melting point °C.
101		Recrystallisation from ethano	60	223-227
102		Filtration	90	114-115
103		Filtration, recrystallisation from propanol	63	>275 (decomposition)

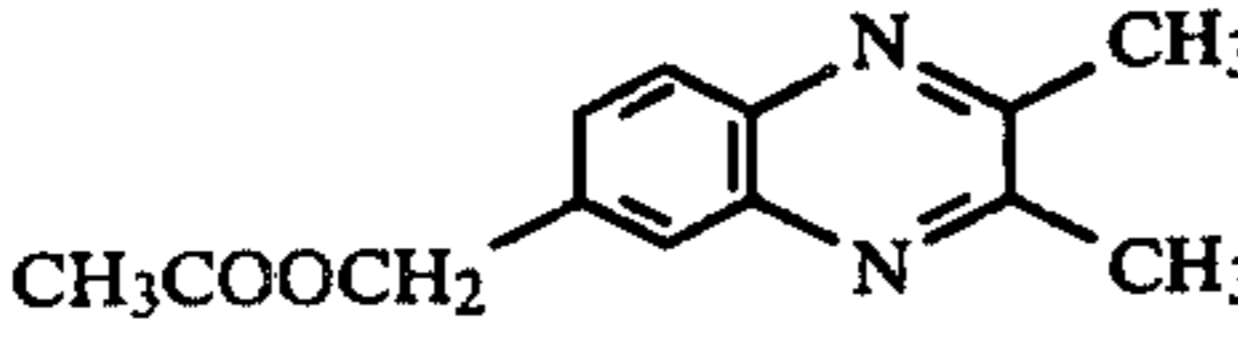
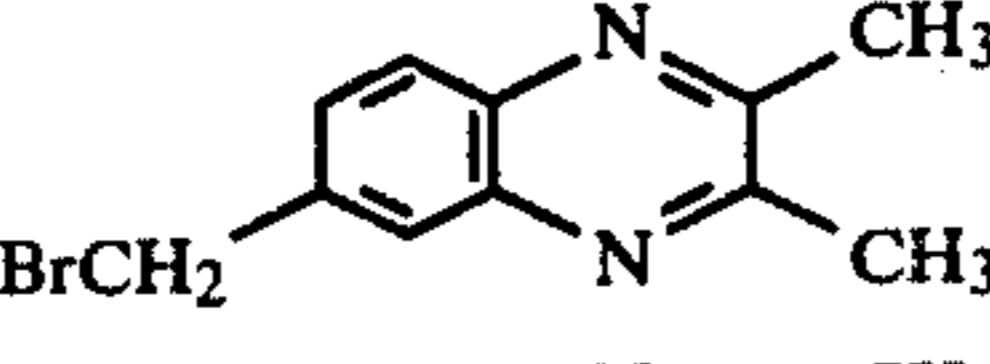
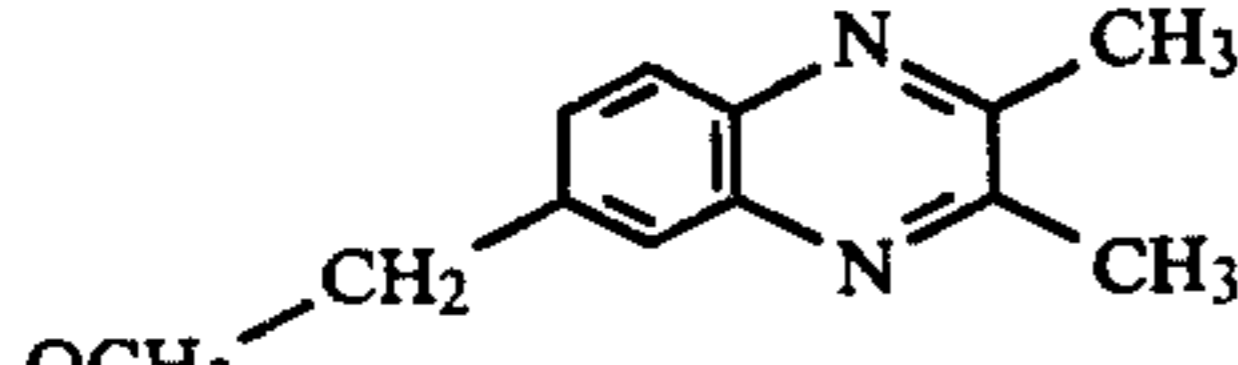
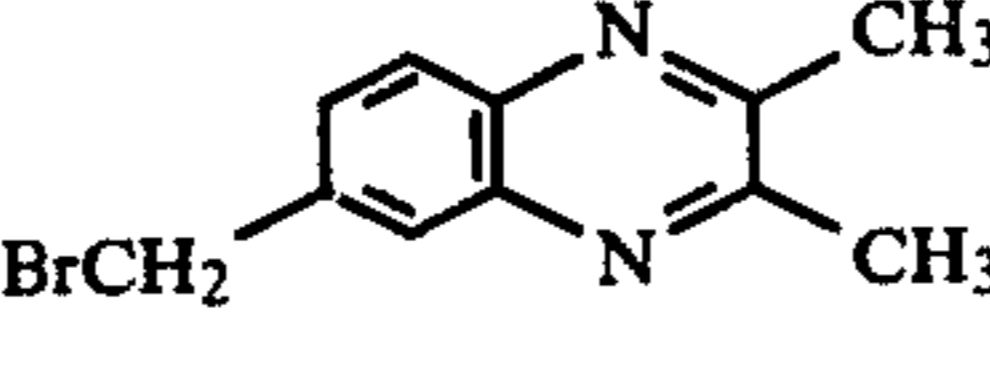
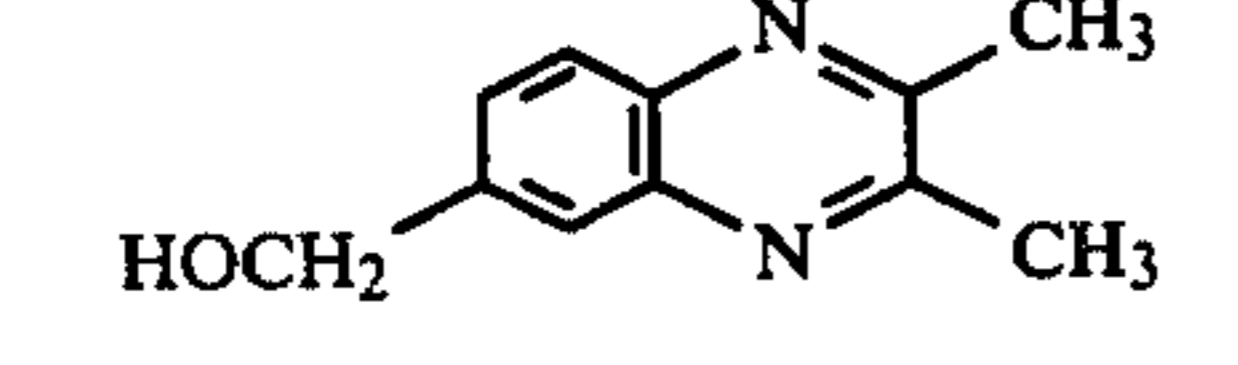
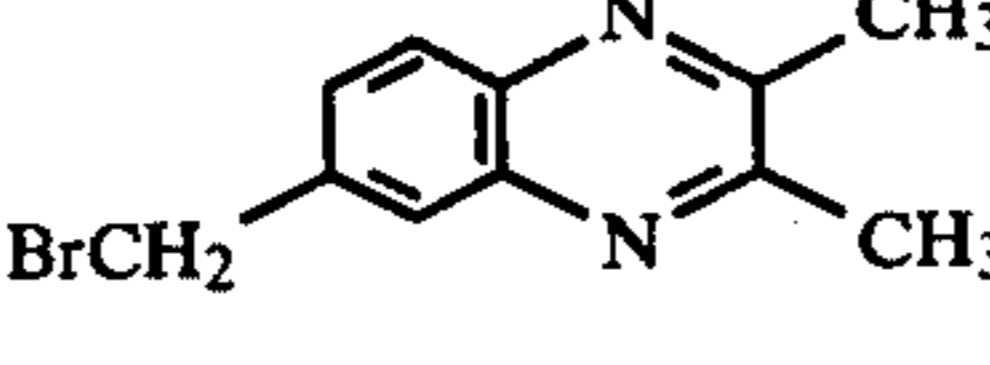
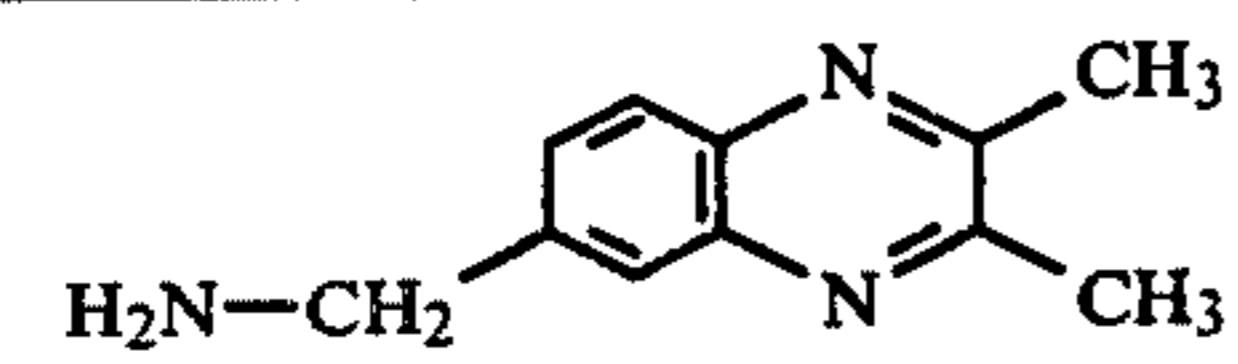
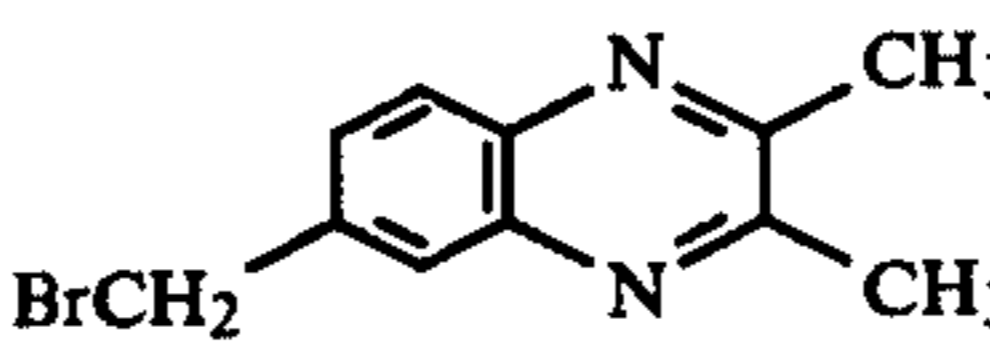
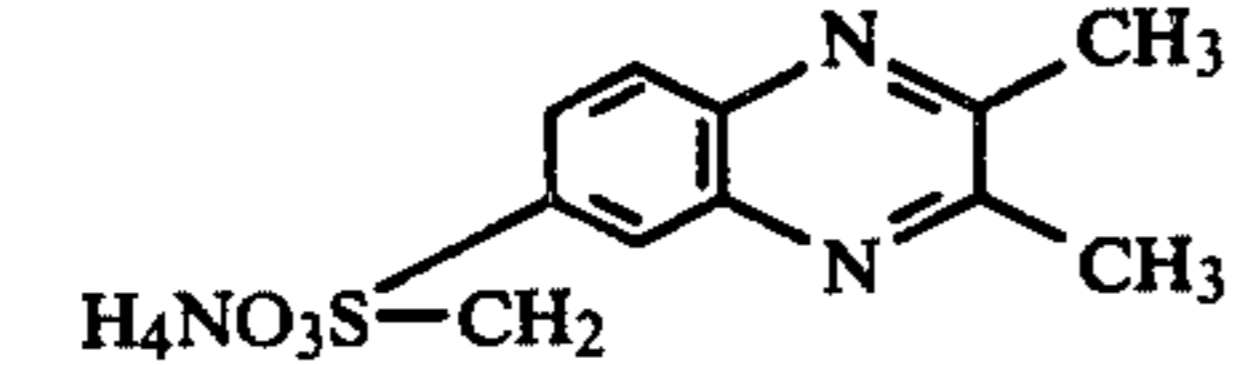
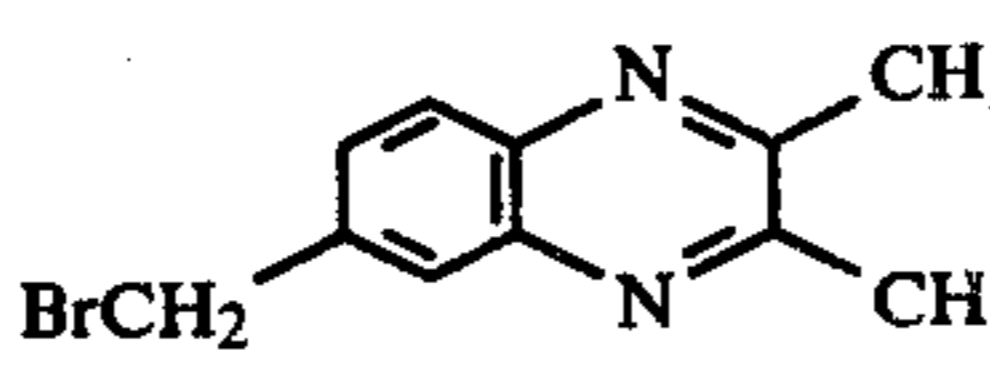
The NMR and infrared spectra of the compounds in this table agree with the indicated structures.

TABLE II

No.	Compound	Starting materials	Diketone	Isolation/purification	Yield %	Melting point °C.
104			(CH ₃ CO) ₂	Filtration	75	226-228
105			(CH ₃ CO) ₂	Recrystallisation from dimethylformamide	80	>275

The NMR and infrared spectra of the compounds in this table correspond to the indicated structures.

TABLE III

No.	Compound	Starting materials	Lewis base solvent	Isolation/purification	Yield %	Boiling point (b.p.)/ melting point (m.p.) °C.
106			CH ₃ COOK ethanol	Chromatography SiO ₂ / CH ₃ COOC ₂ H ₅	57	m.p. 64-68
107			CH ₃ ONa methanol	distillation	60	b.p. 100° C./ 0.2 mm Hg m.p. 58-62
108			H ₂ O/ K ₂ CO ₃ acetonitrile	chromatography SiO ₂ / CH ₃ COOC ₂ H ₅	30	m.p. 101-104
No.	Compound	Starting materials	Lewis base solvent	Isolation/purification	Yield %	Melting point °C.
109			(1) Potassium phthalimide/ dimethylformamide/60° C. (2) N ₂ H ₄ / ethanol (3) H ⁺	Chromatography SiO ₂ Ethyl acetate/ methanol	46	93 (hygroscopic)
110			Na ₂ SO ₃ water	via the free acid (betain) and neutralisation with ammonia	49	300° (decomposition)

The NMR and infrared spectra of the compounds in this table agree with the indicated structures.

Compound (108) has already been described (J.A. Silk, J. Chem. Soc. 1956, 2,058); however, the preparation from the bromomethyl derivative by means of nucleophilic substitution is simpler than the synthesis route described in the literature.

TABLE IV

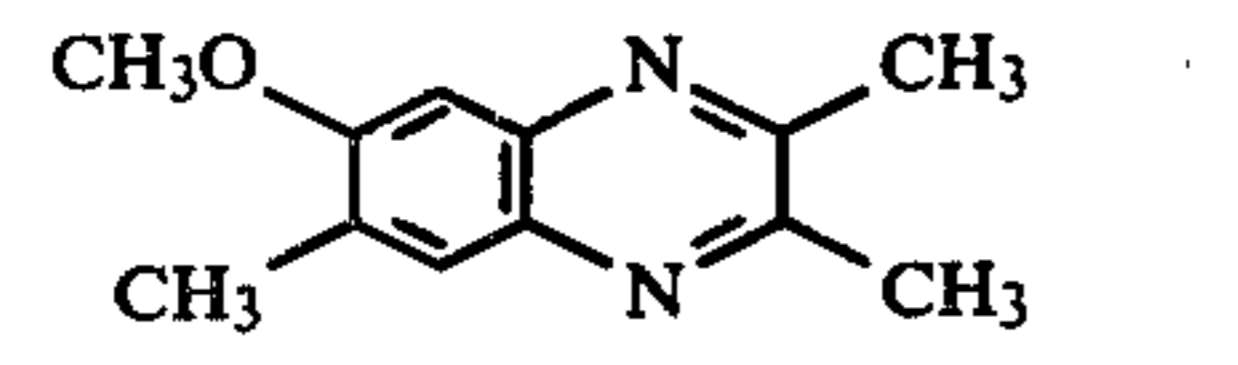
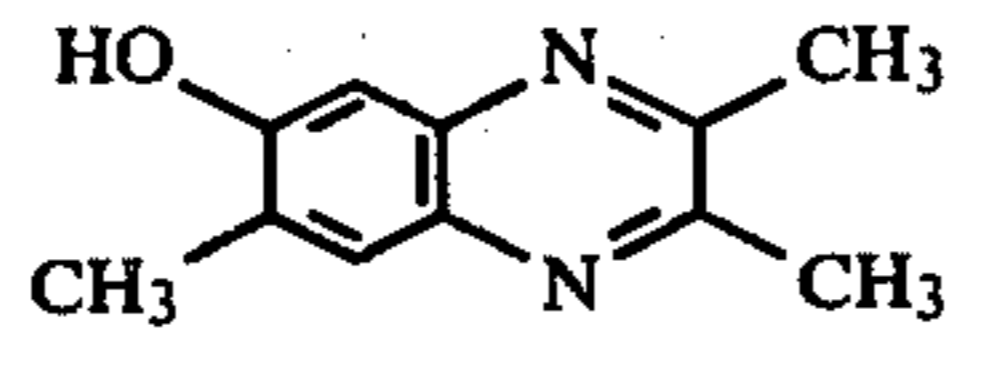
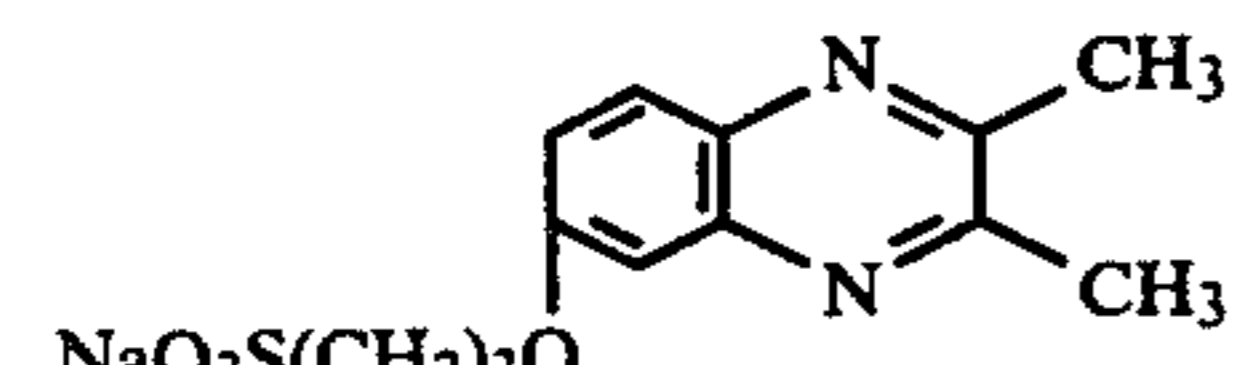
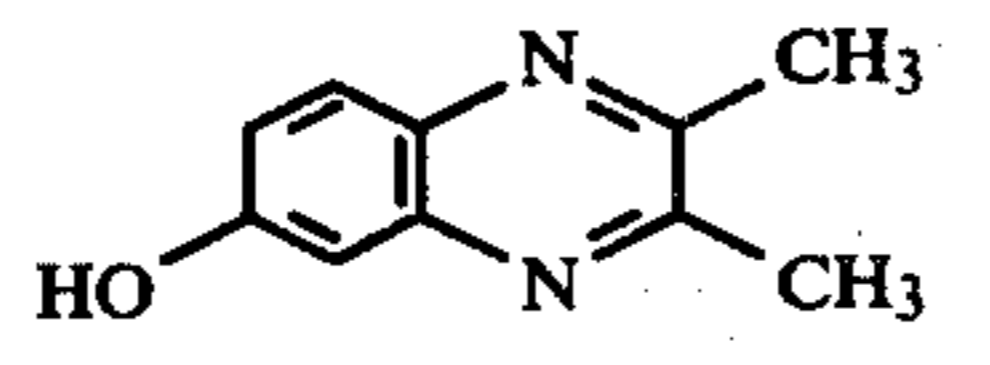
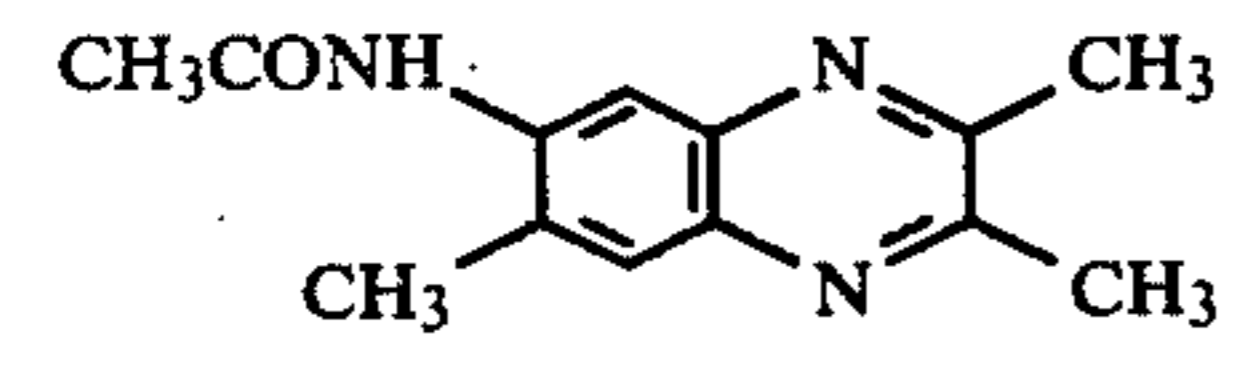
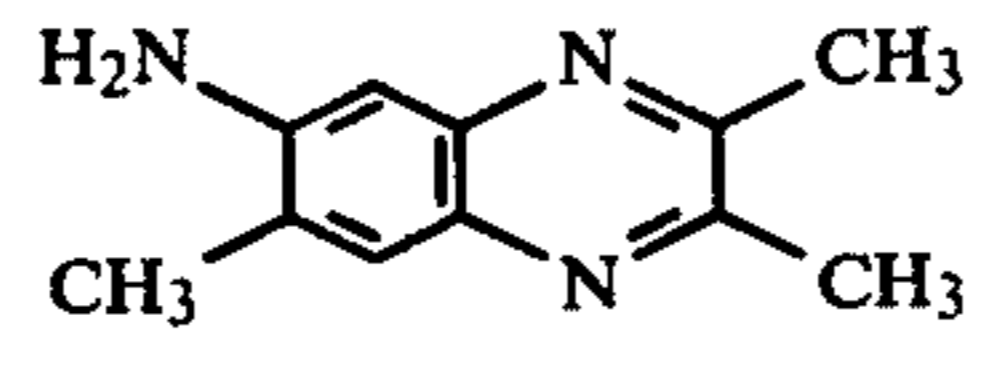
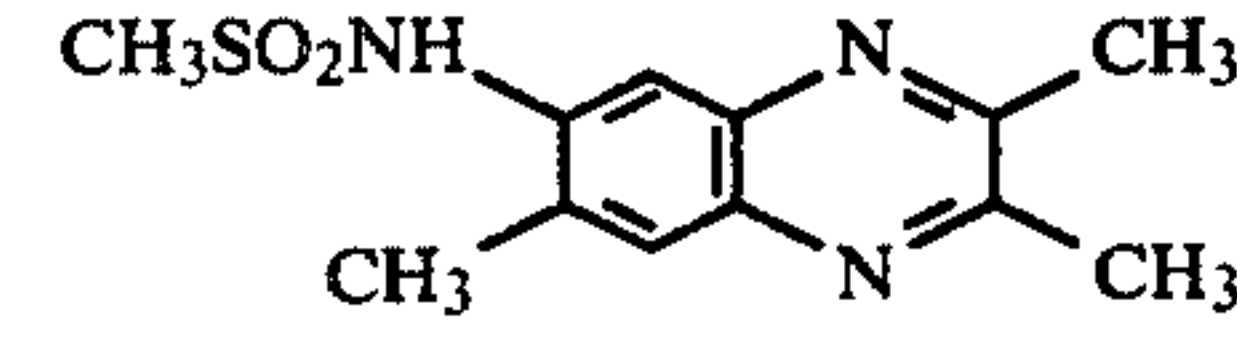
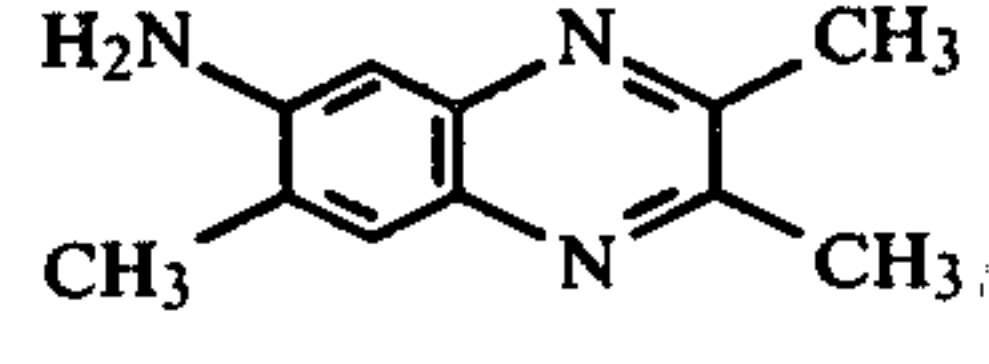
No.	Compound	Starting materials	Alkylating/acylating agent	Isolation/purification	Yield %	Melting point °C.
			(CH ₃) ₂ SO ₄ NaOH/H ₂ O	recrystallisation from ethanol/H ₂ O	55	143-145
112			NaOH/ dimethylformamide	filtration	58	200 (decomposition) crystallises with one mol of H ₂ O
113			acetic anhydride/ toluene	filtration	71	252
114			CH ₃ SO ₂ Cl/ pyridine	via the sodium salt	47	218-219

TABLE IV-continued

No.	Compound	Starting materials	Reagent	Isolation purification	Yield %	Melting point °C.
115			Oleum 10%	Extraction of the ammonium salt with methanol	92	226-240 (decomposition)
116			N-bromosuccinimide/CCl ₄ /azobisisobutyronitrile	Evaporation of the solvent and suspension in n-hexane	55 (yield of crude product 95)	105-107 the crude product contains 5% of a different isomer.

The NMR and infrared spectra of the compounds in this table agree with the indicated structures.

APPLICATION EXAMPLES

EXAMPLE 1

The effectiveness of the new quinoxalines as silver dye bleach catalysts is examined with the aid of single layer coatings of the following composition: 8.2 g of gelatine/m²

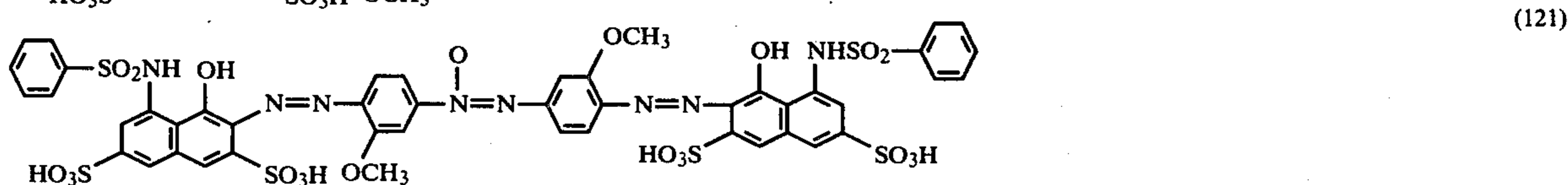
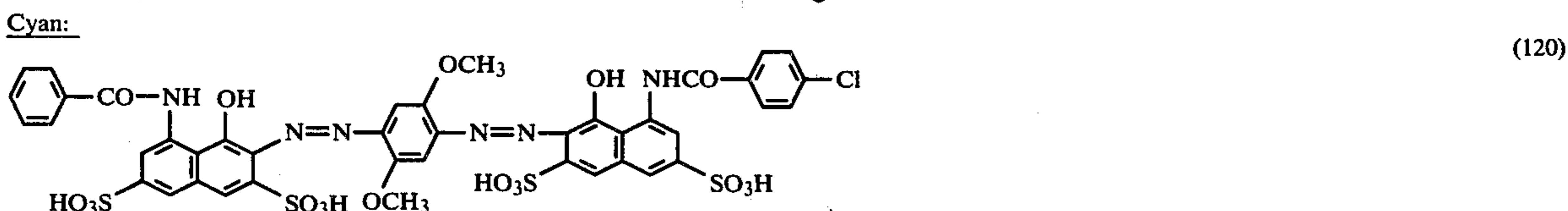
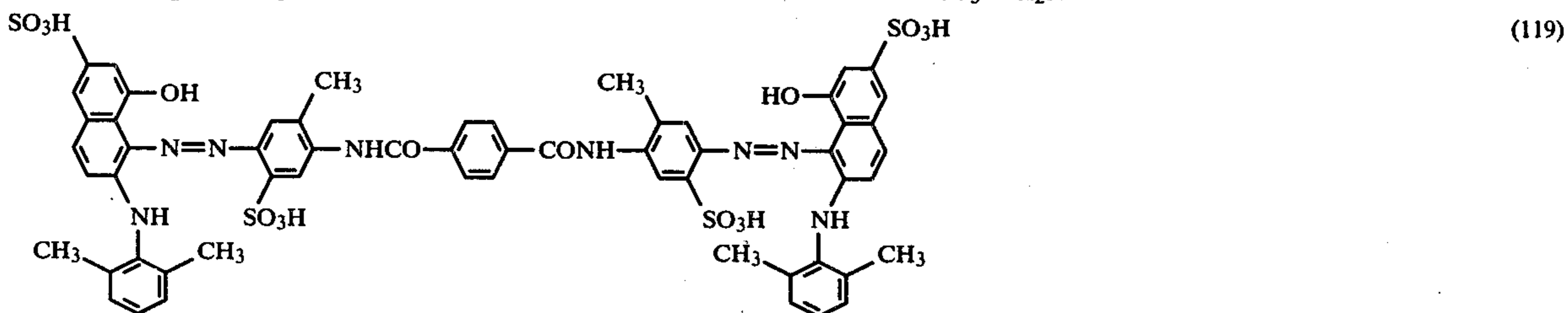
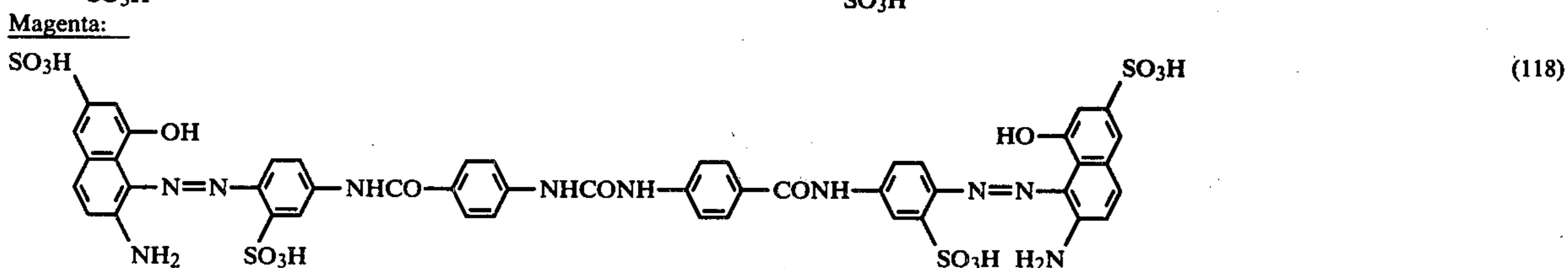
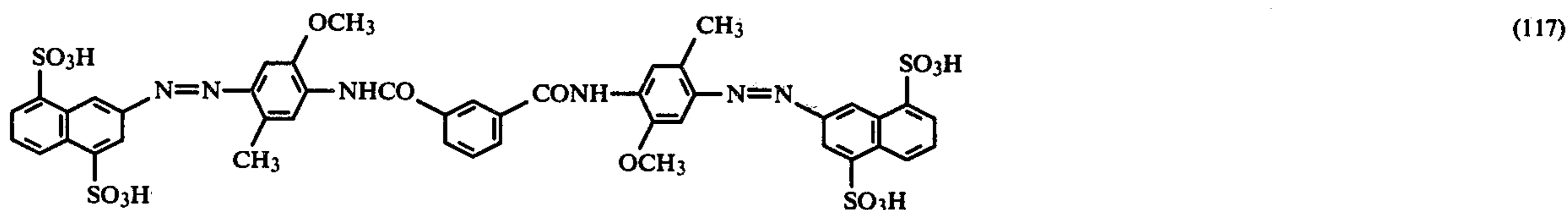
Molar ratio of silver to dyestuff: 44:1

Maximum transmission density of the dyestuff about 1.4.

The silver halide emulsion used is a bromide/iodide emulsion which contains 2.6 mol% of iodine and has not been spectrally sensitised. One of the following dye-

Coatings, which correspond to the above data, on opaque triacetate film are exposed behind a step wedge 15 and then processed at 24° C., as follows:

Developing bath	6 minutes
Washing	4 minutes
Dye bleach bath	7 minutes
Washing	2 minutes
Silver bleach bath	2 minutes
Washing	2 minutes
Fixing bath	8 minutes
Washing	6 minutes
Drying	



A conventional black-and-white developer is used in the developing bath and baths of customary composition are also used as the silver bleach bath and the fixing bath. The dye bleach bath contains the following components: 28 ml of concentrated sulphuric acid, 1 ml of thioglycerol, 9 g of sodium iodide and 1 mmol of the dye bleach catalyst from Table I-III, per liter of solution.

As a result of processing, a sharp yellow or magenta or cyan step wedge is obtained, depending on the dye-stuff.

EXAMPLE 2

Single layer coatings according to Example 1 are exposed behind a step wedge and then processed at 24° C., as follows:

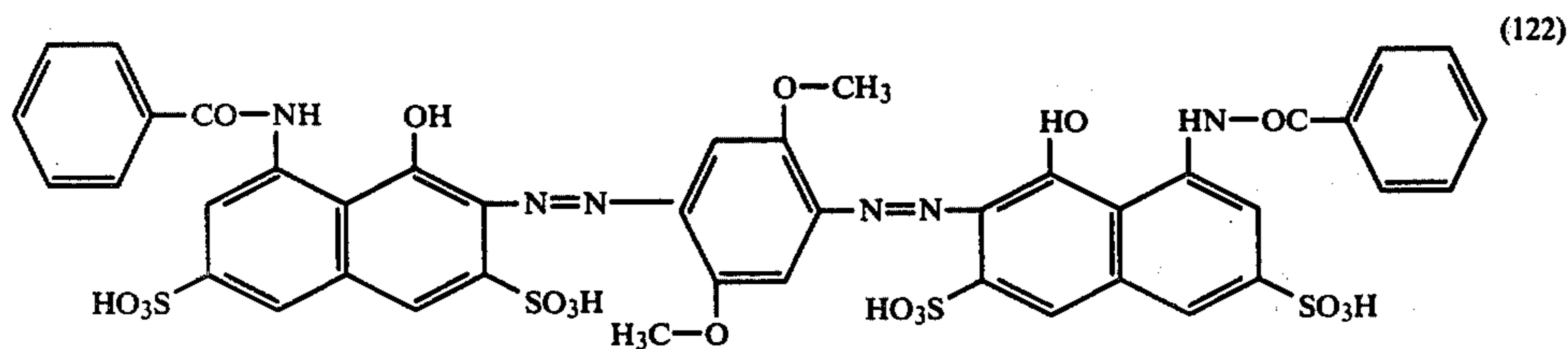
Developing bath	6 minutes
Washing	4 minutes
Bleach bath	6 minutes
Washing	2 minutes
Fixing bath	8 minutes
Washing	6 minutes
Drying	

A conventional black-and-white developer is used as the developing bath and a conventional fixing bath is used as the fixing bath. The bleach bath contains the following components: 28 ml of concentrated sulphuric acid, 1 ml of thioglycerol, 9 g of sodium iodide, 10 mmols of m-nitrobenzenesulphonic acid and 5 mmols of the catalyst of the formula (108), per liter of solution.

As a result of processing, a sharp yellow or magenta or cyan step wedge is obtained, depending on the dye-stuff. Analogous results are also obtained with other combinations of the catalysts from Tables I to III and the oxidising agents of the formula (18).

EXAMPLE 3

A photographic material with three colour layers for the silver dye bleach process is prepared on a cellulose acetate carrier; it contains, in the lowest, red-sensitive layer, the cyan image dyestuff of the formula



in the green-sensitive layer above the preceding layer, the magenta image dyestuff of the formula (118) and in the uppermost, blue-sensitive layer, the yellow image dyestuff of the formula (117).

The image dyestuffs are incorporated into the emulsions so as to give a reflection density of $D=2.0$. The colour layers, containing a total of 0.8 g of Ag/m^2 , are separated by gelatine layers and the total thickness is 15μ .

This material is exposed through a step wedge and then processed as follows:

1. Silver developing bath	
Sodium polyphosphate	2 g/l
Anhydrous sodium sulphite	50 g/l
Hydroquinone	6 g/l
Sodium metaborate	15 g/l
Borax	15 g/l
1-Phenyl-3-pyrazolidinone	0.25 g/l
Potassium bromide	1 g/l
Benzotriazole	0.1 g/l

-continued

2. Bleach bath	
96% strength sulphuric acid	28 ml/l
Thioglycerol	1 ml/l
Sodium iodide	9 g
2-Amino-4-methyl-5-nitrobenzenesulphonic acid (ammonium salt)	5 g/l
Catalyst: compound of the formula (105)	1.1 g/l
3. Fixing bath	
60% strength ammonium thiosulphate	315 ml/l
60% strength ammonium bisulphate	46 ml/l
25% strength ammonia (aqueous solutions each).	20 ml/l
4. Washing	

After drying, a clear neutral grey image of the subject used is obtained, the exposed regions having been bleached to pure white. Similar results are obtained when other combinations of the catalysts from Tables I to III and the oxidising agent of the formula (18) are employed in corresponding amounts.

EXAMPLE 4

A photographic material for the silver dye bleach process is prepared on a pigmented cellulose acetate carrier using the cyan image dyestuff of the formula (122), the magenta image dyestuff of the formula (118) and the yellow image dyestuff of the formula (117).

The material is made up of double layers, as follows (compare German Offenlegungsschrift No. 2,036,918).

blue-sensitive, colourless
blue-sensitive, yellow dyestuff (117)
yellow filter
green-sensitive, colourless
green-sensitive, magenta dyestuff (118)
intermediate layer (gelatine)
red-sensitive, cyan dyestuff (122)
red-sensitive, colourless
carrier, opaque

The image dyestuffs are incorporated into the coatings so as to give a reflection density of $D=2.0$. The total silver content of the three-colour material is 2.0 g of Ag/m^2 and the total thickness of the photographic layers is 22μ .

In an enlarger, an image of a coloured transparency is projected onto the material. Processing is then carried out in accordance with the following instructions (bath temperature 24° C):

1. Silver developing bath: 2 minutes

Composition	
Sodium polyphosphate	1 g/l
anhydrous sodium sulphite	40 g/l
Hydroquinone	10 g/l
Sodium metaborate	20 g/l
Sodium hydroxide	3 g/l
1-Phenyl-3-pyrazolidinone	1 g/l
Potassium bromide	1.5 g/l
Benzotriazole	0.2 g/l

2. Bleach bath: 4 minutes

-continued

Composition	
Sulphamic acid	100 g/l
Ascorbic acid	2 g/l
Ammonium iodide	7 g/l
Sodium salt of m-nitrobenzene sulphonic acid	10 g/l
Catalyst:	
Compound of the formula (112)	3 g/l
3. Fixing bath: 4 minutes	
Composition	
Ammonium thiosulphate	220 g
Sodium metabisulphite	10 g
Sodium sulphite	40 g
4. Washing: 6 minutes	
Total processing time	16 minutes

After drying, a print of the colour transparency is obtained which is true in colour and tonality.

Similar results can be achieved when a bleach bath is used which, for example, is prepared from two liquid concentrates according to the following instructions:

Composition of 1 l of the solution used:	
Water	800 ml
Part A	100 ml
Part B	100 ml
Composition part A:	
96% strength sulphuric acid	20 ml
The sodium salt of m-nitrobenzene-sulphonic acid	7 g
Water to make up to	100 ml
Part B:	
Ethylene glycol monoethyl ether	65 ml
Compound of the formula (112)	3 g
Ascorbic acid	3 g
Potassium iodide	6 g
Water to make up to	100 ml

Other catalysts given in Tables I to III can also be employed as catalysts, in place of the compound of the formula (112) with an equally good result.

EXAMPLE 5

A photographic material containing the dyestuffs according to Example 4 is used.

The image dyestuffs are incorporated into the emulsions so as to give a reflection density of $D=2.0$. The colour layers, containing a total of 0.8 g of Ag/m^2 , are separated by gelatine layers and the total thickness of the 8 layers is 15μ .

This material is exposed in a reproduction camera and then processed in a so-called roll processor. This apparatus consists of 4 tanks, each of 2 liters capacity. The speed of the drive system is so adjusted that the immersion time per tank is 60 seconds. The exposed material passes through the 4 tanks containing the following process solutions and the temperature of the baths is 35°C .

1st Tank - silver developing bath	
Composition	
Sodium polyphosphate	1 g/l
Anhydrous sodium sulphite	40 g/l
Hydroquinone	10 g/l
Sodium metaborate	20 g/l
Sodium hydroxide	3 g/l
1-Phenyl-3-pyrazolidinone	1 g/l
Potassium bromide	1.5 g/l
Benztriazole	0.2 g/l

-continued

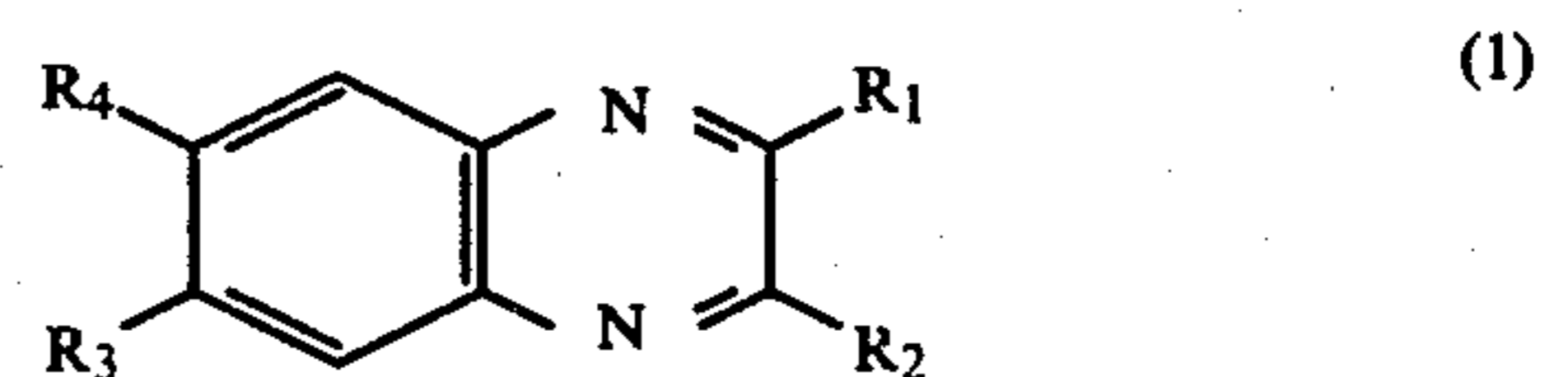
Compound of the formula (103)	0.4 g/l
2nd Tank - bleach bath	
Composition	
96% strength sulphuric acid	20 ml/l
4-Mercaptobutyric acid	1 ml/l
Potassium iodide	10 g
Sodium salt of m-nitrobenzene-sulphonic acid	7 g
Compound of the formula (103)	2 g
3rd Tank - fixing bath	
Composition	
Ammonium thiosulphate	220 g
Sodium metabisulphite	10 g
Sodium sulphite	40 g
4th Tank - washing bath	
Total processing time	5 minutes
(including transport time from tank to tank and with equal dwell time of about 1 minute in the individual tanks).	

After drying, reproductions of the recorded subjects are obtained which are true to nature in colour and tonality. With one filling of the tank it is possible to develop 40 to 60 images $18\text{ cm}\times 24\text{ cm}$ in size in the course of 14 days; the quality of the images is virtually unchanged.

The other compounds given in Tables I to III can also be employed, in place of the compound of the formula (103) with an equally good result.

We claim:

1. Process for the production of colored photographic images by the silver dye bleach process which comprises the steps of imagewise exposing a photographic material containing on a substrate, at least one silver halide emulsion layer with a bleachable dyestuff, then (1) developing the silver image obtained, (2) dye bleaching and silver bleaching said silver image, (3) silver fixing and (4) washing, said dye and/or silver bleaching step being carried out in a bath containing at least one bleach catalyst of the formula

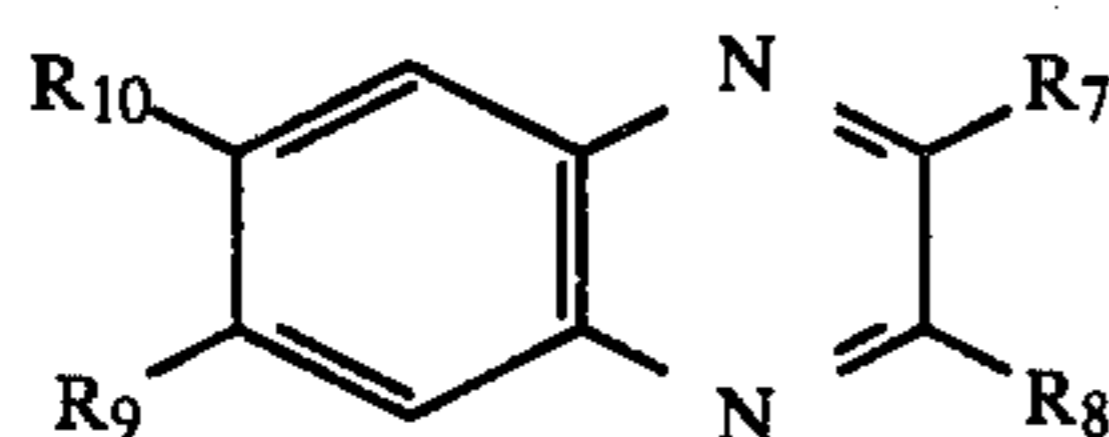


in which R_1 and R_2 independently are alkyl with 1 to 5 carbon atoms, R_3 is alkyl with 1 to 5 carbon atoms, $-\text{CH}_2\text{OR}_5$, $\text{CH}_2\text{NRR}'$, $-\text{CH}_2\text{OCOR}$, $-\text{CH}_2\text{Cl}$, $-\text{CH}_2\text{Br}$, CH_2SR , $-\text{CH}_2\text{O}(\text{CH}_2)_p\text{OR}$, $-\text{CH}_2\text{PO}(\text{OR}_5)_2$, $-\text{CH}_2\text{PO}(\text{OR}_6)_2$, $\text{CH}_2\text{SO}_3\text{R}_6$, $-\text{O}(\text{CH}_2)_m\text{OR}$, $-\text{O}(\text{CH}_2)_p\text{SO}_3\text{R}_6$ or $-(\text{OCH}_2\text{CH}_2)_n\text{OAr}$, R_4 is hydrogen or alkyl with 1 to 5 carbon atoms or alkoxy of 1 to 4 carbon atoms, when R_3 is other than an alkyl radical with 1 to 5 carbon atoms, or R_4 is $-\text{OH}$, $-\text{NRR}'$, $-\text{NHCOR}$, $-\text{NHCOAr}'$, $-\text{NHCOAr}'$, $-\text{NHSO}_2\text{R}_5$ or $-\text{NHSO}_2\text{Ar}'$, R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms, R_5 is alkyl with 1 to 4 carbon atoms, R_6 is hydrogen, an alkali metal cation or $-\text{N}^\oplus(\text{R})_4$, Ar is aryl or sulphonated aryl, Ar' is aryl or substituted aryl, m is 3 or 4, n is 1 to 3 and p is 2 to 4.

2. Process according to claim 1, wherein R_1 and R_2 independently are methyl or ethyl, R_3 has the meaning indicated in claim 1 and R_4 is hydrogen or alkyl with 1 to 5 carbon atoms when R_3 is other than alkyl with 1 to 5 carbon atoms, or is $-\text{OH}$, $-\text{NRR}'$, $-\text{NHCOR}$ or

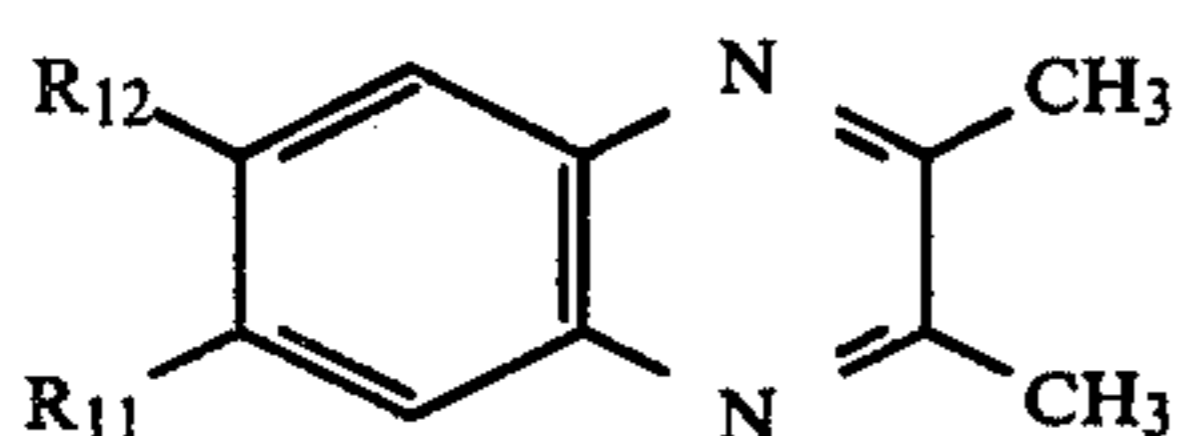
—NHSO₂R₅, in which R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms.

3. Process according to claim 1, wherein the bleach catalyst corresponds to the formula



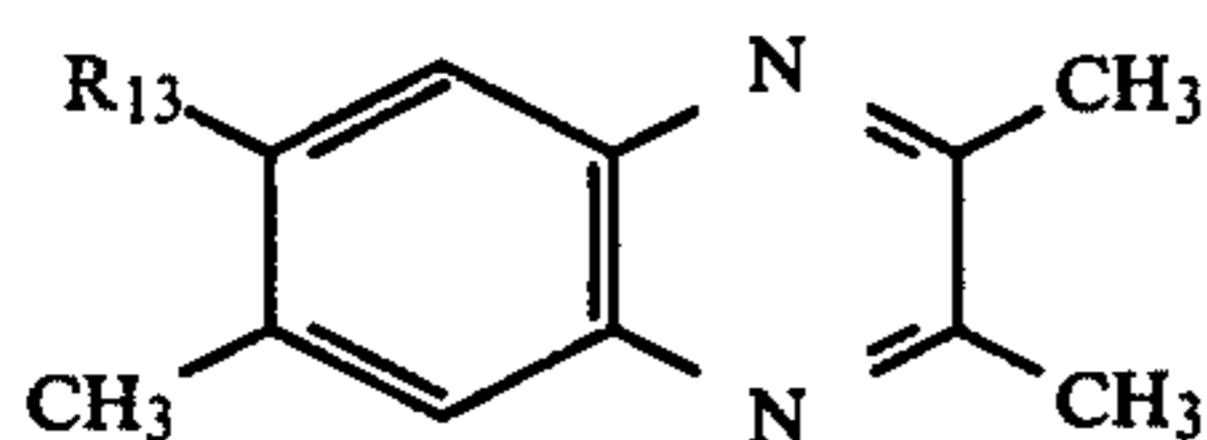
in which R₇ and R₈ independently are methyl or ethyl, R₉ is alkyl with 1 to 5 carbon atoms and R₁₀ is —OH, NRR', —NHCOR or —NHSO₂R and R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms.

4. Process according to claim 3, wherein the bleach catalyst corresponds to the formula



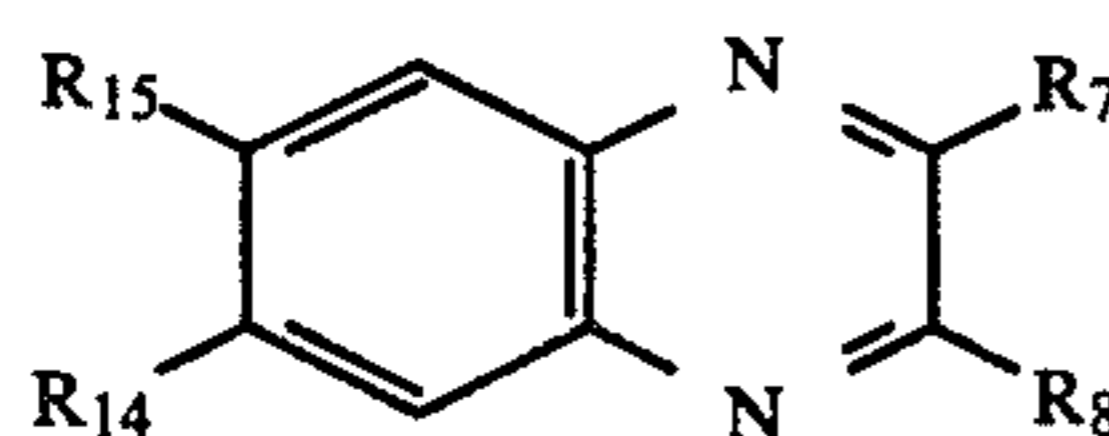
in which R₁₁ is methyl or ethyl and R₁₂ is —OH, —NR''R''', —NHCOCH₃ or —NHSO₂CH₃ and R'' and R''' independently are hydrogen or methyl.

5. Process according to claim 4, wherein the bleach catalyst corresponds to the formula



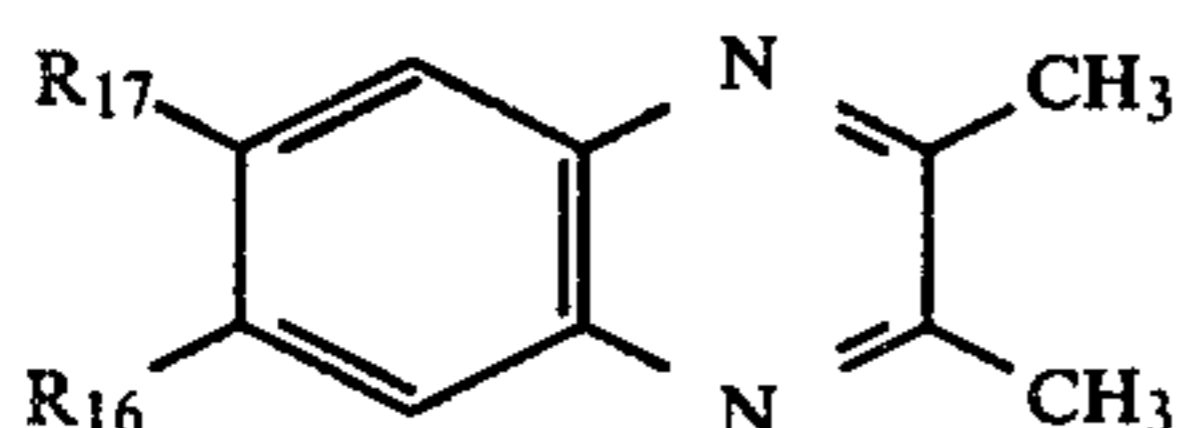
in which R₁₃ is —OH, NH₂ or —NHCOCH₃.

6. Process according to claim 1, wherein the bleach catalyst corresponds to the formula



in which R₇ and R₈ independently are methyl or ethyl, R₁₄ is —CH₂OR₅, —CH₂NRR', —CH₂OCOR, —CH₂Cl, —CH₂Br, —CH₂SR, —CH₂O(CH₂)_pOR, —CH₂PO(OR₅)₂, —CH₂PO(OR₆)₂, —CH₂SO₃R₆, —O(CH₂)_mOR, —O(CH₂)_pSO₃R₆ or —(OCH₂CH₂)_nOAr, R₁₅ is hydrogen or alkyl with 1 to 5 carbon atoms, —OH or —OCH₃, R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms, R₅ is alkyl with 1 to 4 carbon atoms, R₆ is hydrogen, an alkali metal cation or —N[⊕](R)₄, Ar is aryl or sulphonated aryl, m is 3 or 4, n is 1 to 3 and p is 2 to 4.

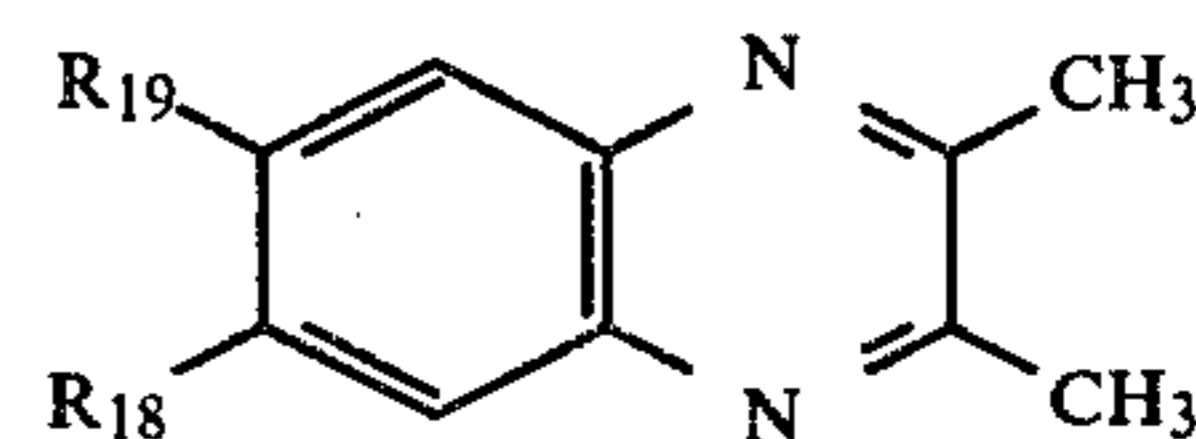
7. Process according to claim 6, wherein the bleach catalyst corresponds to the formula



in which R₁₆ is —CH₂Cl, —CH₂Br, —CH₂OCH₃, —CH₂COOH, —CH₂OCOCH₃, —CH₂NR''R''', —CH₂SO₃R₆, —CH₂O(CH₂)_pOH, —CH₂O(CH₂

)_pOCH₃, —O(CH₂)_pSO₃R₆ or —(OCH₂CH₂)_nOAr, R₁₇ is hydrogen, hydroxyl, methyl, ethyl or methoxy, R₆ is hydrogen, an alkali metal cation or —N[⊕](R)₄ and R is hydrogen or alkyl with 1 to 4 carbon atoms, R'' and R''' independently are hydrogen or methyl, Ar is aryl or sulphonated aryl, n is 1 to 3 and p is 2 to 4.

8. Process according to claim 7, wherein the bleach catalyst corresponds to the formula

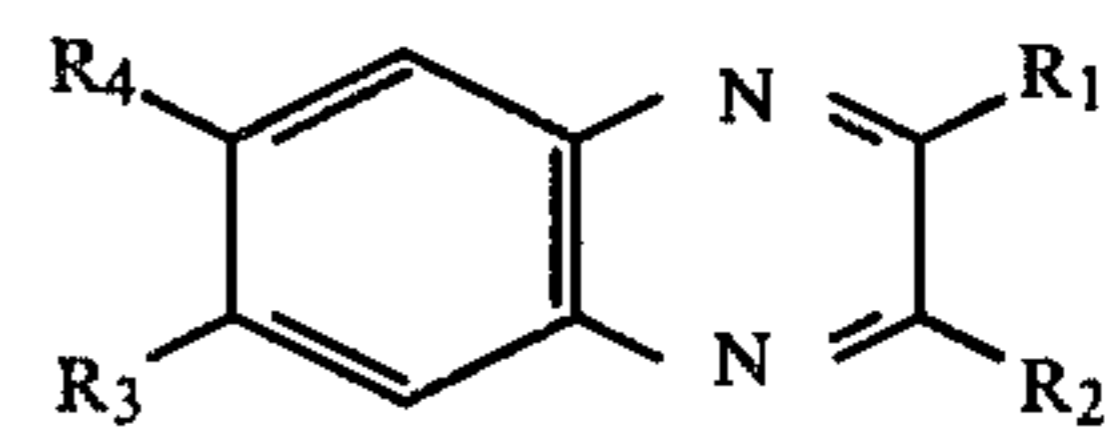


in which R₁₈ is —CH₂Br, —CH₂OCH₃, —CH₂COOH, —CH₂OCOCH₃, —CH₂NH₂, —CH₂SO₃R₆, —O(CH₂)_pSO₃R₆, —(OCH₂CH₂)_nOC₆H₅ or —(OCH₂CH₂)_nOC₆H₄SO₃R₆, R₁₉ is hydrogen, methyl, hydroxyl or methoxy, R₆ is hydrogen, an alkali metal cation or —N[⊕](R)₄, R is hydrogen or alkali of 1 to 4 carbon atoms, n is 1 to 3 and p is 2 to 4.

9. Process according to claim 1, wherein the treatment stages (1) to (4) are used in the sequence (1) to (4), wherein the bleach bath (2) for the combined dye bleaching and silver bleaching contains (a) a strong acid, (b) a water-soluble iodide, (c) a water-soluble oxidising agent, (d) an anti-oxidant and (e) a bleach catalyst and (f) optionally a bleach accelerator and the entire processing, from entry into the first bath (1) to leaving the final bath, is carried out at temperatures of 20° to 90° C.

10. Process according to claim 9, wherein the entire processing, from entry into the first bath (1) to leaving the final bath, takes at most 10 minutes and the dwell time in the individual processing tanks is at most 2 minutes.

11. Aqueous formulation for dye bleaching and/or silver bleaching which contains (a) a strong acid, (b) a water-soluble iodide, (c) a water-soluble oxidising agent, (d) an anti-oxidant, (e) a bleach catalyst and, optionally, (f) a bleach accelerator, wherein the bleach catalyst is a quinoxaline of the formula



in which R₁ and R₂ independently are alkyl with 1 to 5 carbon atoms, R₃ is alkyl with 1 to 5 carbon atoms, —CH₂OR₅, —CH₂NRR', —CH₂OCOR, —CH₂Cl, —CH₂Br, —CH₂SR, —CH₂O(CH₂)_pOR, —CH₂PO(OR₅)₂, —CH₂PO(OR₆)₂, —CH₂SO₃R₆, —O(CH₂)_mOR, —O(CH₂)_pSO₃R₆ or —(OCH₂CH₂)_nOAr, R₄ is hydrogen or alkyl with 1 to 5 carbon atoms or alkoxy of 1 to 4 carbon atoms when R₃ is other than an alkyl radical with 1 to 5 carbon atoms or R₄ is —OH, —NRR', —NHCOR, —NHCOAr', —NHSO₂R₅ or —NHSO₂Ar', R and R' independently are hydrogen or alkyl with 1 to 4 carbon atoms, R₅ is alkyl with 1 to 4 carbon atoms, R₆ is hydrogen, an alkali metal cation or —N[⊕](R)₄, Ar is aryl or sulphonated aryl, Ar' is aryl or substituted aryl, m is 3 or 4, n is 1 to 3 and p is 2 to 4.

12. Aqueous formulation according to claim 11, which contains 0.5 to 5.0 g/l of the bleach catalyst.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,202,698
DATED : May 13, 1980
INVENTOR(S) : Jan et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

- Column 1, line 31, $-\text{N}(\text{R})_4$ should be $-\text{N}(\text{R})_4^{\oplus}$.
Column 1, line 36 "armyl" should be "amyl".
Column 3, line 29 " Ch_2OCH_3 " should be " CH_2OCH_3 ".
Column 11, line 43, "hydrosulphite" should be "hyposulphite".
Column 17, Table IV, Column 1, under "No" delete the complete line.
Column 26, line 1 " $-\text{O}(\text{CH}_2)\text{PSO}_3\text{R}_6$ " should be " $-\text{O}(\text{CH}_2)_p\text{SO}_3\text{R}_6$ ".

Signed and Sealed this

Twenty-sixth Day of August 1980

[SEAL]

Attest:

SIDNEY A. DIAMOND

Attesting Officer

Commissioner of Patents and Trademarks